

UNIVERSITY OF ALBERTA

DETERMINATION OF SILVER(I) IN THE PRESENCE SILVER(0) USING EDTA
TITRATION

BY

ASHA PHILIPS ALEX



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of MASTER OF SCIENCE.

DEPARTMENT OF CHEMISTRY

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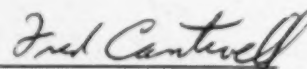
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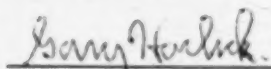
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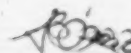
The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled DETERMINATION OF SILVER(I) IN THE PRESENCE SILVER(0) USING EDTA TITRATION submitted by ASHA PHILIPS ALEX in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE.



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ABSTRACT

Silver coated materials have been well studied for their antimicrobial activities. The release of silver from silver coatings may be in the form of elemental silver, silver oxide or silver chloride. To study the biological action of silver coatings a better understanding of different forms of silver present in the solution is necessary.

The underlying idea for the studies that has been done in this project was to determine Ag(I) in the presence of Ag(0). Ag(I) was reacted with potassium tetracyanonickelate(II) in ammoniacal media to release a stoichiometric quantity of nickel. The latter was determined by a titration with EDTA. It is hard to locate the visual end point when the concentration of Ag(I) present is lower than 0.001M due to the gradual color change. Therefore for low concentration of Ag(I), the titration was done spectrophotometrically at pH 11.8 using murexide as indicator. Absorbance was plotted vs. milliliters of titrant and the end point was determined by the intersection of two linear portions of the graph. A suitable blank correction was calculated from a knowledge of the exact weight of solid potassium tetracyanonickelate(II) added. The equilibrium formation constant of nickel - murexide complex was determined spectrophotometrically in order to calculate the proper blank correction. An average value of $4.3 \times 10^{15} \pm 0.4 \times 10^{15} \text{ M}^{-1}$ was obtained. This procedure allows determination of Ag(I) in the form of hydrated ion as well as in the form of silver halides. An added benefit of this procedure is that a blank titration is not necessary.

In an air free atmosphere the same titration was performed on $\text{Ag}(0)$ particles. It was demonstrated that under this condition $\text{Ag}(0)$ was not titrated by EDTA. Only the $\text{Ag}(I)$ in the thin silver oxide layer coating of the $\text{Ag}(0)$ particles was titrated. When a mixture of $\text{Ag}(I)$ and $\text{Ag}(0)$ was titrated the concentration of $\text{Ag}(I)$ found was in agreement with the known value of $\text{Ag}(I)$ added. The procedure is simple, fast and precise.

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This is dedicated to my father Dr. T.P Thomas and mother Mrs. Aswathi Thomas, who will always be my inspiration.

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SYMBOLS AND ABBREVIATIONS

SYMBOL	DESCRIPTION
A	Absorbance
AA	Atomic absorption spectrophotometry
A_{400}	Absorbance at 400 nm
A_{500}	Absorbance at 500 nm
A_{550}	Absorbance at 550 nm
Ag(0)	Silver in (0) oxidation state
Ag(I)	Silver in (+1) oxidation state
C_{Ag}	Total concentration of silver that is not bound to cyanide
[CN ⁻]	Concentration of cyanide ion
C_{NH_3}	Total concentration of ammonia
C_{Ni}	Total concentration of nickel that is not bound to cyanide
$C_{Ni, blank}$	Blank correction i.e. concentration of nickel that is not bound to cyanide in blank solution
$C_{Ni, Total}$	Total concentration of nickel
EDTA	Ethylene diammine tetraacetic acid
[H ₂ In ³⁺]	Concentration of free murexide

K_1, K_2, K_3	Stepwise formation constants for nickel hydroxide complexes
K'_1	Equilibrium constant for the reaction between nickel cyanide complex and silver
K'_2	Equilibrium constant of the reaction between $[\text{Ag}(\text{NH}_3)_2]^+$ and cyanide
$K_{\text{Ag}(\text{CN})_2}$	Equilibrium constant of the reaction between silver and cyanide
$K_{\text{Ag-EDTA}}$	Stability constant of Ag-EDTA complex
$K_{\text{D,Ni}(\text{CN})_4}$	Dissociation constant of tetracyanonickelate complex
$K_{\text{Ni-H}_2\text{In}}$	Equilibrium constant of reaction between nickel and murexide
$[\text{Ni}^{+2}]$	Concentration of free nickel(+2) ion
$[\text{Ni-H}_2\text{In}^-]$	Concentration of nickel-murexide complex
Ni-Mur	Nickel-murexide complex
M_{EDTA}	Molarity of EDTA
T	Transmittance
V	Initial volume of sample solution
Vol_{EDTA}	Volume of EDTA
a	Absorbance index
b	Pathlength
c	Concentration of light absorbing species

v	Volume of titrant added
$\alpha_{\text{Ni,NH}_3}$	Fraction of nickel free from ammonia
$\alpha_{\text{Ni,OH}}$	Fraction of nickel free from hydroxide
β_1 - β_6	Overall formation constants of nickel-ammine complexes
β_1' , β_2'	Overall formation constants of silver-ammine complexes
ϵ	Molar absorptivity
$(\epsilon_{\text{Ni-H}_2\text{In}})_{400}$	Molar absorptivity of nickel-murexide complex at 400 nm
$(\epsilon_{\text{Ni-H}_2\text{In}})_{500}$	Molar absorptivity of nickel-murexide complex at 500 nm
$(\epsilon_{\text{Ni-H}_2\text{In}})_{550}$	Molar absorptivity of nickel-murexide complex at 550 nm
γ	Charge of the metal
λ	Wavelength

CHAPTER 1

DETERMINATION OF Ag(I) IN THE PRESENCE OF Ag(0)

1.1 INTRODUCTION

Silver was the subject of many investigations by chemists of the nineteenth century. Its chemistry, which is not complex, was studied extensively and knowledge of it was well established. Silver is an ubiquitous metal of industry, present in medicines and sea water, in alloys found in the communication industry and on the dining table, in photographic film, metallurgical by-products and in soil.

Silver occurs naturally in several oxidation states. The most common are elemental silver and the monovalent silver ion. Silver can be determined by a variety of analytical methods. For the determination of silver in ore grade samples, spectrophotometric methods using organic reagents such as dithiozone [1,2,3], p-dimethylaminobenzylidene rhodanine [2,3,4] or pyrogallol red [5] are widely used. For trace silver analysis, the most widely used analytical technique is atomic absorption spectrometry. The ease of operation, sensitivity, reproducibility and high specificity makes it the first choice as an analytical method for the determination of silver [6,7]. For routine repetitive analysis, volumetric or potentiometric methods are also used [8].

The majority of the recent methods have been developed to determine trace quantities of silver. In this project we are proposing a quantitative measurement of Ag(I) in the presence of Ag(0).

1.2 INDIRECT DETERMINATION OF SILVER(I)

The usual methods for the determination of silver and copper in metallurgical products are time consuming and critically dependent upon conditions which are sometimes difficult to achieve. Volumetric procedures employing ethylene diammine tetraacetic acid (EDTA) have found wide applications. The stability constant of Ag-EDTA complex ($\log K=7.2$) [4] is too small to permit a direct titration with a complex forming indicator. However Ag(I) can be determined indirectly through an exchange reaction with tetracyanonickelate, $[\text{Ni}(\text{CN})_4]^{-2}$ (9-14) whereby an equivalent amount of nickel is set free which can be titrated with EDTA using murexide [15 - 20] or thymolphthalexone and dimethyl yellow [18] or dimethyl glyoxime [1,21] as indicators.

The exchange also takes place quantitatively with sparingly soluble silver salts so that precipitates obtained during the course of separation can be submitted to titration [9]. On this basis, in addition to silver, the halogens can also be titrated after being precipitated as silver halides.

When working with a low concentration of silver ions, it is hard to locate the endpoint visually due to the gradual colour change. A photometric titration technique

eliminates [13,17,22] this difficulty and increases the range of this method.

Another indirect method to determine silver has been developed which is based on the release of zinc from its sulphide in the presence of silver halides and titration of Zn(II) with EDTA [23].

1.3 SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF SILVER(I)

The spectrophotometric determination of silver is usually preceded by reaction with dithiozone [24], 4-(2-quinolylazo) phenol [25], 2-(4-amino-3-(1,2,4-triazolylazo)naphthol-4-sulfonate [26], 4,4 -bis(dimethylamino)thiobenzophenone [27], ammonium 2-cyano-3-iminodithiobutyrate [28], or ammonium (2,3 -dihydroxypyridyl-4 -azo)benzene-4-arsonate [29]. However most of these methods lack sensitivity, selectivity and/or reproducibility. Pyrogallol red is used as a reagent for the spectrophotometric determination of silver ions in dilute solutions [30], but this method has a drawback due to the halide interference. Di-2-naphthylthiocarbazone(DNZ) has been used as a titrant in spectrophotometric extractive titration for silver [31]. In addition to the halide interference, the lower stability of DNZ solution and lack of reliable equilibrium constants to enable prediction of optimum conditions are the major disadvantages.

Rhodanine derivatives have also found wide application in the determination of silver [32-36]. However, many problems are associated with their use, including solubility of reagents and instability of the developed colours [37]. Recently a spectrophotometric determination of silver has been developed with 5-(2,4-dihydroxybenzylidene) rhodanine in the presence of cationic surfactant [38]. But halide and cyanide ions interfered in the determination.

The procedure for determining silver utilising the exchange reaction of silver with potassium tetracyanonickelate is simple and the results are reproducible and accurate. It can be done even in the presence of halide ions. Gedansky and Gordon [22] utilised this reaction to extend the determination of silver to the micro scale in which the released amount of nickel is determined spectrophotometrically with EDTA using murexide as the indicator.

1.4 PRINCIPLES OF PHOTOMETRIC TITRATIONS

In a photometric titration, the substance titrated, the titrant or the product must absorb radiation at the wavelength used. The fundamental law of monochromatic light absorption underlying photometric titration is the Bouguer-Lambert-Beer law $A = -\log T = abc$, in which A = absorbance(optical density), T = transmittance, a = absorbance index, b = path length through the absorbing medium and c = concentration of light absorbing species. Since absorbance is linearly proportional to the concentration of absorbing ions,

an appreciable break will often be obtained in a photometric titration [39, 40]. A plot of absorbance against volume of titrant yields two straight lines that intersect at the end point. Figure 1.1 illustrates typical photometric titration curves.

If an indicator is present during the initial addition of titrant (EDTA), the "free" metal is complexed (Figure 1.2). In a plot of absorbance versus millilitres this part of the titration curve will have a zero slope or only a slight one, depending on whether the formation of the metal-EDTA complex is accompanied by a colour change or not (part a, Figure 1.2). When all the free metal has combined with the EDTA, the next increments of titrant will begin to remove the metal from the indicator complex. This step is accompanied by a much larger change in absorbance (part b, Figure 1.2). When all the metal is removed from the indicator, any further addition of EDTA will not change the absorbance, except by dilution (part c, Figure 1.2). There would be two breaks observed in this case. One break would be observed in the region where all the free metal is titrated with EDTA and the other would be in the part of the graph where all the metal - indicator complexes are titrated with EDTA. After that break there would not be any change in the absorbance. That will account all forms of metal that is titrated by the EDTA. Hence the point on the curve where the indicator complex is fully titrated is taken for the end point determination.

If the indicator exists in different protonated forms, the pH must be selected so that only one species predominates at that pH. Murexide is used as the indicator for the indirect determination of silver. It exists in different protonated form depending on the pH. Nickel reacts with all species of indicator murexide. Therefore pH should be selected

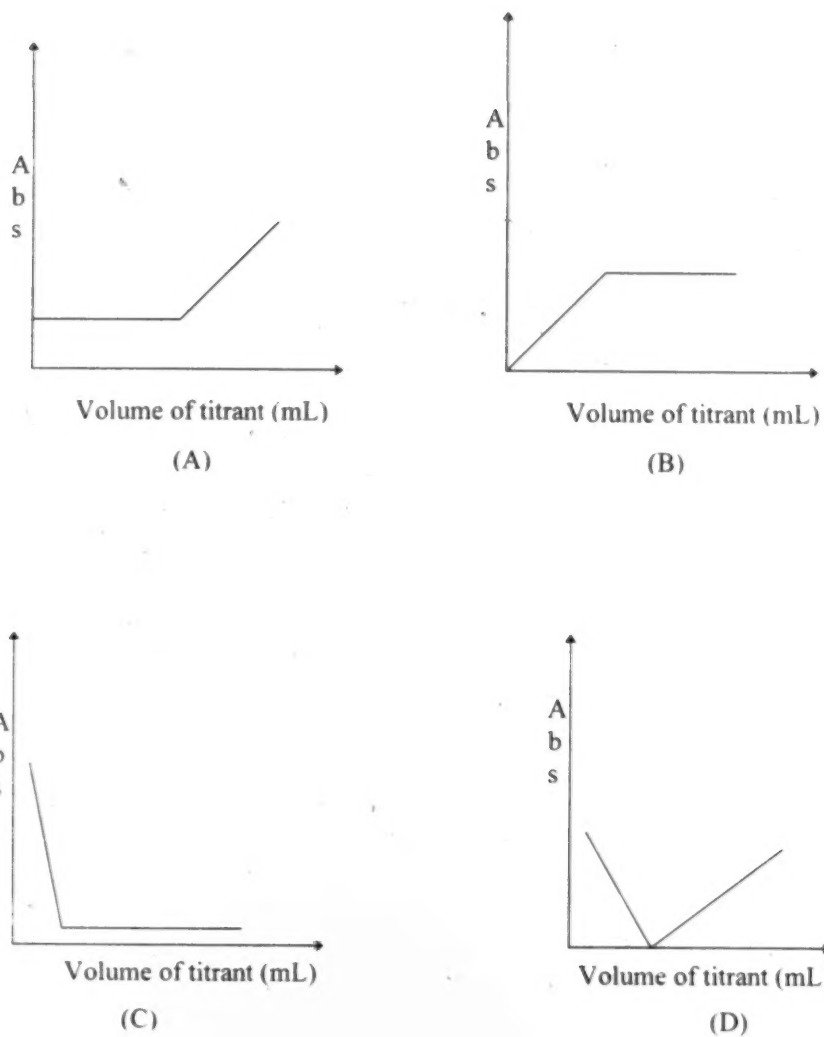


Figure 1.1: Several schematic photometric titration curves. (A) Titrant absorbs radiation at wavelength of measurement; (B) product absorbs, titrant does not; (C) substance titrated absorbs; titrant does not; (D) substance titrated and titrant absorb, product does not.

so that only one form of the indicator exists at that particular pH.

It must be kept in mind that even though Beer's law may be obeyed, two straight lines are obtained only when dilution by titrant is properly accounted. During titration the volume of solution continuously increases. Accordingly plots of absorbance against volume bend toward the volume axis and the end point intersection would be in error if the dilution effect were not taken into account. Correction for dilution is accomplished by multiplying the absorbance by the factor $\frac{(V + v)}{V}$ where V is the initial volume of the sample solution and v the volume of the titrant added. The dilution effect can be made negligible by adding fairly concentrated solution of titrant.

For a photometric titration to be practical, the reaction must fulfil the usual requirements of speed and of known stoichiometry. If the plot in the vicinity of the end point is curved, the difficulty can be overcome by drawing two linear lines somewhat distant from the equivalent point and the end point is located at the point of intersection as shown in Figure 1.2.

In spectrophotometric titration of silver using murexide as indicator, absorbance of murexide in the free form and complexed form (Ni-Mur complex) allows photometric titration and the end point is obtained by plotting absorbance vs volume of titrant. Details of the procedure are discussed in chapter 5.

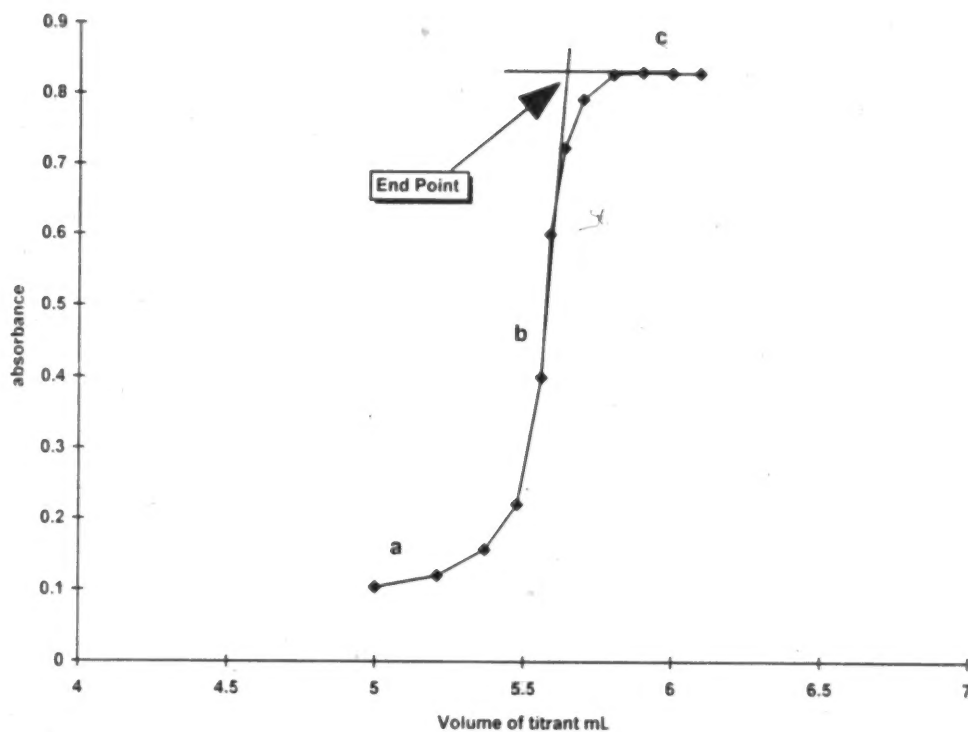


Figure 1.2 Typical photometric titration curve (scale divisions arbitrary). Absorbance is monitored at a wavelength where the free indicator absorbs more strongly than the metal-indicator complex. The end point is determined by extrapolating two straight lines in the region b and c and the point of intersection is taken as the end point.

1.5 RESEARCH OBJECTIVES

A large number of metals, particularly the heavy metals, have germicidal properties when they are brought into contact with germ-containing liquids [41]. Silver has been known for years for its broad spectrum antimicrobial and antiinflammatory properties [42,43]. Colloidal silver was used in wound antisepsis and in combination with citrate salts for skin infections. One to two percent silver nitrate was employed almost 100 years ago for the treatment of ophthalmia neonatorum [42]. This property of the lethal effect of metal concentration is called the oligodynamic effect (from the Greek, oligos = few; and dynamics = power). It may also be mentioned at this point that it appears necessary to restrict the application of this term oligodynamic activity to certain processes in which low concentrations of metal ions are involved [41], in contradistinction to the well known lethal action of the salts of heavy metals, such as sublimate, copper sulphate, arsenic etc. at high concentrations, although the physiological effect of such metal poisons may be in many cases identical with the consequences of the oligodynamic phenomena [41]. In view of practical application, it appears that silver is best suited as an oligodynamic material because of the extremely slight solubility of most of its salt, which in fact renders it almost impossible for large concentrations of silver ions to occur in higher organisms. Medical application of silver involves silver-coated nylon fabrics that are used to treat and manage postoperative debridement of wounds in cases of severe chronic osteomyelitis [44,45]. In surgical practice silver foil or plates are

used for insertion into wounds or replacement of missing bone fragments [46,47].

The exact antimicrobial mode of action of silver is not known, but several possible mechanisms have been suggested. The oligodynamic activity of silver is attributed to the inactivation of enzymes via silver complexes with electron donors (thiols, carboxylates, amines, phosphates, hydroxyl, imidazoles, indoles) [42]. For silver to be toxic in low doses, the ionic form of the metal must come into direct contact with metabolically active sites, such as cell membranes of micro organisms [48]. The lipid phase of the cell membrane appears to play an important role in the adsorption of silver ions by living cells. Binding of -SH groups seems to be the principal mechanism by which silver ions inhibit enzyme activity [49].

When the metal oxidises, the rate at which metal ions enters into the solution can be found by quantitative measurement. It is wise to know the concentration of silver in metallic form and ionic form to get a better understanding of the oligodynamic effect of silver. For trace analysis of silver, the most widely used method is atomic absorption spectrometry due to its advantages of high selectivity and sensitivity . But it measures the total amount of silver instead of differentiating between Ag(I) and Ag(0) . It is difficult to find the concentration of Ag(I) in the presence of Ag(0) . The major objective of this project is to achieve that goal. In the proposed method Ag(I) is determined quantitatively in the presence of Ag(0) . A portion of the silver solution containing both Ag(0) and Ag(I) is taken for EDTA titration in the absence of air to avoid the oxidation of Ag(0) . The EDTA titration result will determine Ag(I) quantitatively.

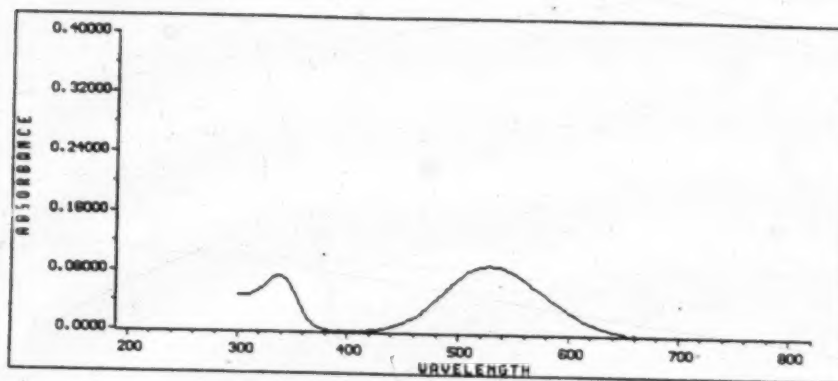
CHAPTER 2

DETERMINATION OF STABILITY CONSTANT OF THE NICKEL -MUREXIDE COMPLEX

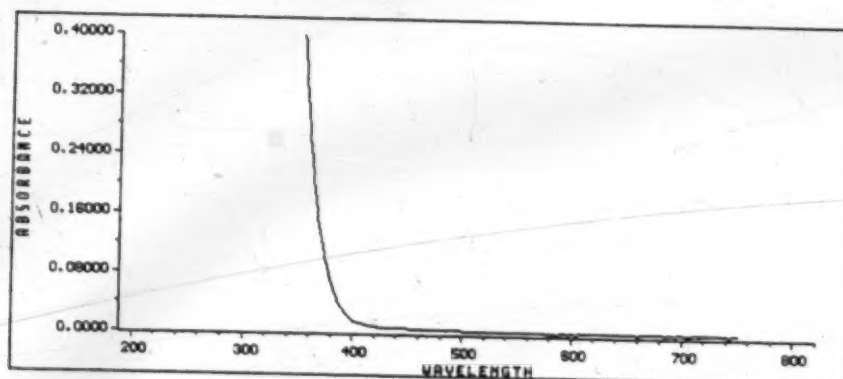
2.1 INTRODUCTION

In ammoniacal medium, Ag(I) reacts with potassium tetracyanonickelate(II) to release a stoichiometric quantity of nickel. Gordon and Gedansky [22] used this reaction for the determination of Ag(I) in which nickel is determined spectrophotometrically by EDTA titration using murexide as indicator. When murexide was added prior to the addition of silver to an ammoniacal solution of tetracyanonickelate, a peak at 442 nm shows that a compound is formed. It was also found that the absorbance of free indicator at 550 nm gets considerably lower when $K_2Ni(CN)_4$ was added to an ammoniacal solution of murexide.

Individual spectra of $K_2Ni(CN)_4$, murexide, $Ni(NO_3)_2$, $Ni(NO_3)_2$ and murexide, a solution containing $K_2Ni(CN)_4$ and murexide and a solution containing $K_2Ni(CN)_4$, $AgNO_3$ and murexide at pH 11.8 are shown in Figure 2.1 to Figure 2.3. There is no peak at 442 nm for $K_2Ni(CN)_4$ or murexide or $Ni(NO_3)_2$ solution at pH 11.8 but it can be

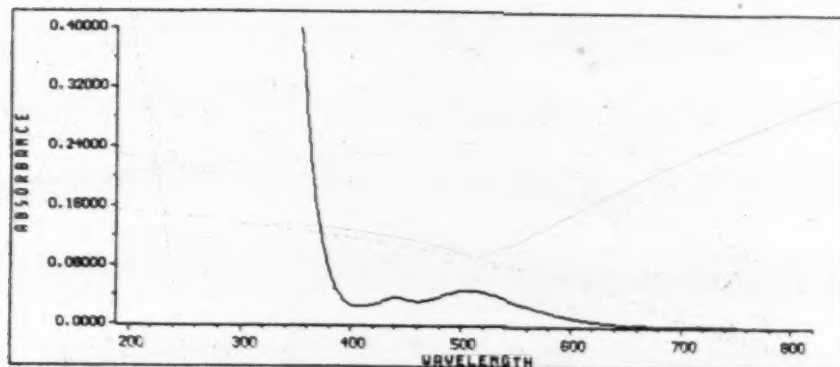


(A)

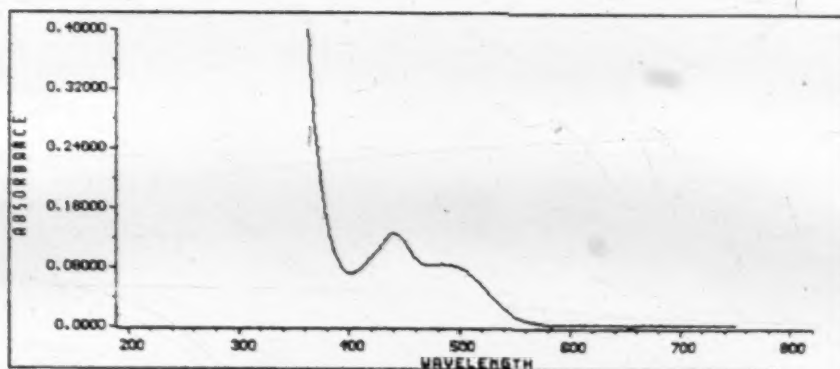


(B)

Figure 2.1: (A) Spectrum of murexide (~ 8 mg of murexide in 50 mL nanopure water containing 1.4M NH_3 buffer; pH 11.8); (B) Spectrum of potassium tetracyanonickelate (~50 mg of $\text{K}_2\text{Ni}(\text{CN})_4$ in 50 mL nanopure water containing 1.4M NH_3 buffer; pH 11.8).

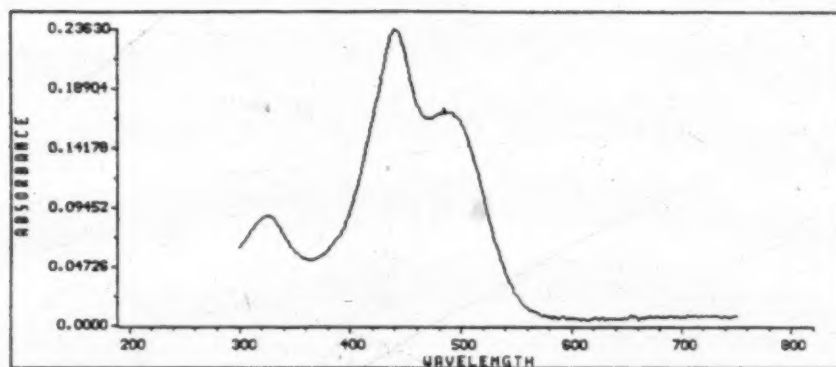


(C)

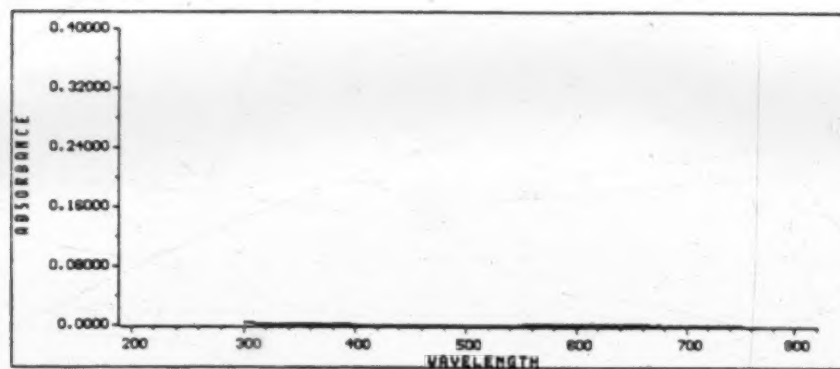


(D)

Figure 2.2: (C) Spectrum of $\text{K}_2\text{Ni}(\text{CN})_4$ and murexide (~ 50 mg of $\text{K}_2\text{Ni}(\text{CN})_4$ and ~ 8 mg of murexide in 50 mL nanopure water containing 1.4M NH_3 buffer; pH 11.8) ; (D) Spectrum of 50 mL solution containing AgNO_3 , $\text{K}_2\text{Ni}(\text{CN})_4$ and murexide ($\sim 10^{-4}\text{M}$ Ag^+ containing ~ 50 mg of $\text{K}_2\text{Ni}(\text{CN})_4$, ~ 8 mg of murexide and 1.4M NH_3 buffer; pH 11.8).



(E)



(F)

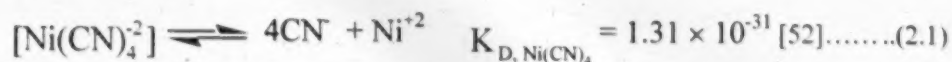
Figure 2.3: (E) Spectrum of $\text{Ni}(\text{NO}_3)_2$ and murexide (10^{-4} M Ni^{+2} solution having ~ 8 mg of murexide and 1.4M ammonia buffer; pH 11.8; (F) Spectrum of $\text{Ni}(\text{NO}_3)_2$ (of 10^{-4} M Ni^{+2} solution buffered by 1.4M ammonia; pH 11.8).

found in solutions containing $\text{Ni}(\text{NO}_3)_2$ and murexide, solution containing $\text{K}_2\text{Ni}(\text{CN})_4$ and murexide or a solution containing $\text{K}_2\text{Ni}(\text{CN})_4$, AgNO_3 and murexide at pH 11.8. This shows that the peak at 442 nm is due to nickel-murexide complex. When working with a low concentration of $\text{Ag}(\text{I})$, we cannot neglect this formation. The lowering of absorbance of murexide after the addition of potassium tetracyanonickelate (Figure 2.2.C vs Figure 2.1.A) showed that a considerable amount of indicator was bound by $\text{Ni}(\text{II})$. In order to account for this, the stability constant of the nickel-murexide must be determined.

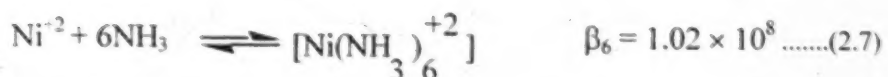
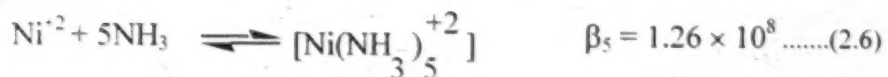
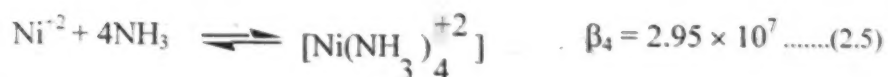
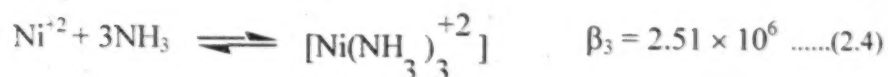
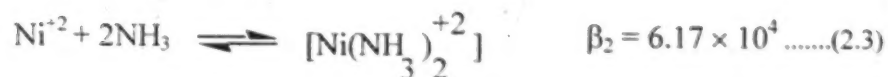
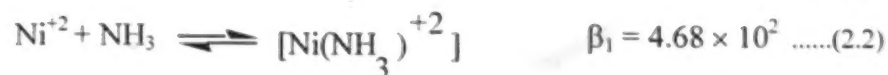
The conditional constant for nickel- murexide at pH 10 using ammonia-ammonium chloride buffer is reported in the literature [50,51], but the concentration of ammonia is not provided in the literature. However, ammonia also complexes Ni^{+2} . Therefore it was considered desirable to find the stability constant of nickel - murexide. For that purpose, a Ni^{+2} solution was added to the murexide solution at pH 11.8 at which $[\text{Ni}_5\text{H}_2\text{In}^-] < [\text{H}_2\text{In}^{3-}]$. The equilibrium concentration of nickel-murexide and free murexide was monitored spectrophotometrically. Then the stability constant of the nickel-murexide complex was calculated.

2.2 THEORY

Potassium tetracyano nickelate in the solution has the following equilibrium:



In the presence of ammonia and murexide, the equilibrium of equation (2.1) will shift to the right. The extent of dissociation depends on the stability constant of nickel with ammonia and murexide.



Values for the overall constants (β) were taken from [52,53].

The concentration of all nickel species that are not bound to the cyanide in the blank solution containing ammonia and murexide and no silver i.e. the blank correction is represented as $C_{\text{Ni, blank}}$

$$C_{\text{Ni, blank}} = [\text{Ni}^{+2}] + [\text{Ni}(\text{NH}_3)^{+2}] + [\text{Ni}(\text{NH}_3)_2^{+2}] + [\text{Ni}(\text{NH}_3)_3^{+2}] + [\text{Ni}(\text{NH}_3)_4^{+2}] + \\ [\text{Ni}(\text{NH}_3)_5^{+2}] + [\text{Ni}(\text{NH}_3)_6^{+2}] + [\text{Ni-H}_2\text{In}^-] \dots\dots\dots(2.8)$$

At pH 11.8 murexide is represented as H_2In^{-3} and the reaction between nickel and murexide at pH 11.8 can be represented as $\text{Ni}^{+2} + \text{H}_2\text{In}^{-3} \rightleftharpoons \text{Ni-H}_2\text{In}^-$

$$K_{\text{Ni-H}_2\text{In}} = \frac{[\text{Ni-H}_2\text{In}^-]}{[\text{Ni}^{+2}][\text{H}_2\text{In}^{-3}]} \dots\dots\dots(2.9)$$

Rearranging equation (2.9) gives, $[\text{Ni-H}_2\text{In}^-] K_{\text{Ni-H}_2\text{In}} = [\text{H}_2\text{In}^{-3}] [\text{Ni}^{2+}]$. Hence to calculate $[\text{Ni-H}_2\text{In}^-]$, the $K_{\text{Ni-H}_2\text{In}}$ must be determined.

2.2.1 EFFECT OF pH ON MUREXIDE

Murexide is an ammonium salt of purpuric acid and is probably the first metallochromic indicator to be employed in EDTA titration [17, 50]. Murexide is a pH indicator and its reddish violet anion is shown in Figure 2.4 (a) [55,56]. The negative charge on the anion is actually spread over all four oxygen atoms in the central part of the molecule. Free purpuric acid which is yellow in color, is obtained only in the presence of strong mineral acids ($\text{H}_4\text{In}^- \rightarrow \text{H}_5\text{In}$, $\text{pK} \sim 0$) [55] and it is very unstable in that it is almost immediately hydrolysed. In consequence, the violet solutions below pH 3 are bleached more and more rapidly as the acidity increases.

As the pH increases two more protons are removed from the imido groups. Up to pH = 8, it is represented as H_4In^- (red violet), from pH 8-10 it is H_3In^{2-} (violet; H_4In^-

$\rightarrow \text{H}_3\text{In}^{2-}$, $\text{pK} = 9.2$), and above pH 10 it is H_2In^{3-} (blue - violet; $\text{H}_3\text{In}^{2-} \rightarrow \text{H}_2\text{In}^{3-}$, $\text{pK} = 10.5$) [17,50,51,55,57,59]. The color changes are due to the progressive displacement of protons from imido group. The last two hydrogens in H_2In^{3-} are not ionisable.

The ability of murexide to form metal complexes is easily understood, since two five membered chelate rings are produced by simultaneous coordination through the central nitrogen atom and two oxygen atoms. One of the tautomeric forms of the nickel-murexide complex at pH 11.8 is shown in Figure 2.4(b). Murexide forms a variety of 1:1 metal complexes $\text{MH}_4\text{In}^{\gamma-1}$, $\text{MH}_3\text{In}^{\gamma-2}$, $\text{MH}_2\text{In}^{\gamma-3}$ [55] where γ is the charge of the metal. At pH 11.8 nickel forms almost exclusively the NiH_2In^- complex with murexide.

The stability constants of calcium and lanthanides with murexide are well studied at pH 6 [60]. The thermodynamics and kinetics of reaction between Ni^{+2} and the murexide indicator have been studied over the pH range 4.0-7.3 in aqueous solutions [58,61] and a kinetic study of the exchange reaction of nickel(II) and silver-EDTA complexes was also carried out [62].

2.2.2 DETERMINATION OF STABILITY CONSTANT

The stability constant for nickel- murexide complex is given by equation (2.9). In the presence of ammonia, most of the free metal would be bound to the buffer. This binding reduces the concentration of free metal $[\text{Ni}^{+2}]$.

$$[\text{Ni}^{+2}] = \{C_{\text{Ni}} - [\text{Ni-H}_2\text{In}]\} \times \alpha_{\text{Ni,NH}_3} \dots\dots\dots(2.10)$$

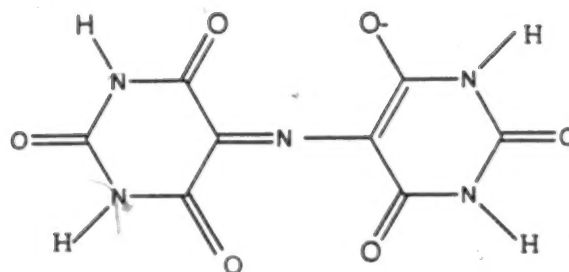
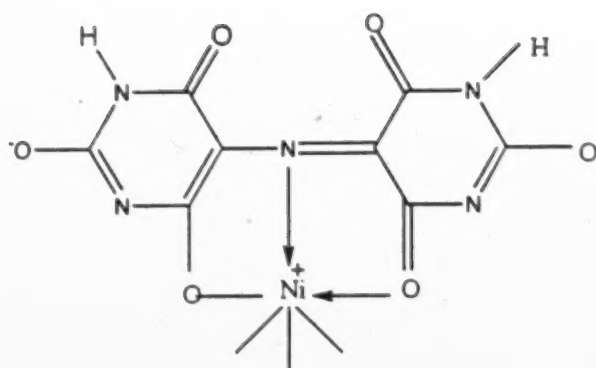
(A) Murexide (H_4In^{3-})(B) $\text{Ni} - \text{H}_2\text{In}^-$

Figure 2.4: (A) Structure of murexide (H_4In^{3-}); (B) Structure of nickel-murexide complex ($\text{Ni} - \text{H}_2\text{In}^-$).

where, $[\text{Ni}^{+2}]$ = Concentration of free nickel, C_{Ni} = Concentration of nickel before the reaction, $[\text{Ni-H}_2\text{In}]$ = Concentration of nickel-murexide complex, $\alpha_{\text{Ni,NH}_3}$ = Fraction of nickel that is free from ammonia.

One could find the concentration of each species at equilibrium spectrophotometrically, knowing the molar absorptivity of each species. Molar absorptivities of murexide and nickel-murexide complex $\text{Ni-H}_2\text{In}^-$ were found individually by plotting absorbance vs. concentration of each species, using NANOpureTM water as reference. Obeying Beer's law, the slope would give ϵ , the molar absorptivity of each species. The choice of wavelengths was influenced by the fact that at 400 nm murexide (H_2In^{3-}) has no absorbance and between 500-550 nm there was an appreciable molar absorptivity difference between the two colored species of the indicator (H_2In^{3-} and $\text{Ni-H}_2\text{In}^-$).

$$A_{400 \text{ nm}} = (\epsilon_{\text{Ni-H}_2\text{In}})_{400} \times [\text{Ni-H}_2\text{In}^-] \times b \dots\dots\dots(2.11)$$

$$A_{550 \text{ nm}} = \{(\epsilon_{\text{Ni-H}_2\text{In}})_{550} \times [\text{Ni-H}_2\text{In}^-] \times b + (\epsilon_{\text{H}_2\text{In}})_{550} \times [\text{H}_2\text{In}^{3-}] \times b\} \dots\dots\dots(2.12)$$

Where $A_{400 \text{ nm}}$ is the absorbance at 400 nm, $A_{550 \text{ nm}}$ = absorbance at 550nm;

$(\epsilon_{\text{Ni-H}_2\text{In}})_{400}$ = molar absorptivity of $\text{Ni-H}_2\text{In}^-$ at 400 nm ; $(\epsilon_{\text{Ni-H}_2\text{In}})_{550}$ = molar

absorptivity of $\text{Ni-H}_2\text{In}^-$ at 550 nm ; $(\epsilon_{\text{H}_2\text{In}})_{550}$ = molar absorptivity of H_2In^{3-} at 550nm;

$[\text{Ni-H}_2\text{In}^{-3}]$ = concentration of Ni-H₂In complex ; $[\text{H}_2\text{In}^{-3}]$ = concentration of free H₂In⁻³ species ; b = pathlength. Using equations (2.11) and (2.12) $[\text{H}_2\text{In}^{-3}]$ can be determined.

2.3 EXPERIMENTAL

2.3.1 REAGENTS AND CHEMICALS

All reagents were AnalaR grade. NiSO₄ · 7 H₂O and KCN were purchased from Aanachemia chemical company. Murexide and ammonia were from BDH Chemicals and Ni(NO₃)₂ was from Caledon. Ni(NO₃)₂ solution was prepared by weighing accurately, the desired amount of nickel nitrate and dissolving it in nanopure water.

The indicator was prepared by mixing about 0.1 g of solid murexide with 10 g of solid KNO₃. This 'indicator mixture' was used through out the experiments. All experiments were carried out at pH 11.8 by adding 5 mL of concentrated ammonia (14.5M) to 45 mL of sample solution. Therefore final concentration of ammonia in 50 mL of sample solution was always about 1.4M.

A NANOpure™ system (Barnstead, model # D4751) was used throughout the experiment to purify water used for sample preparation. All glassware was soaked in diluted HNO₃ and rinsed with NANOpure™ water (nanopure water) prior to being used. A 20 mL pipette was used for delivering silver solution and it is calibrated prior to the use.

2.3.2 PREPARATION OF POTASSIUM TETRACYANONICKELATE(II)

The potassium tetracyanonickelate(II) which was prepared as follows [15,17]. To 50 ml distilled water, 25 g of analytical grade $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved and 25 g of solid potassium cyanide was added portionwise, with agitation. (Caution: use a fumehood). The solution turned yellow and a white precipitate of potassium sulphate separated from it. A 100 mL volume of 95% ethanol was gradually added, with stirring, the precipitated potassium sulphate was filtered off with suction, and washed twice with 2 mL ethanol. The filtrate was concentrated at about 70°C and stirred frequently when the crystals commenced to separate. When the crystalline mass became thick (without evaporating completely to dryness), it was allowed to cool and the crystals were mixed with 50 mL ethanol. Crystals were then separated by suction filtration and washed twice with 5 mL portions of ethanol.

The fine yellow crystals were spread in thin layers on an absorbent paper, and allowed to stand for 2-3 days in the air, adequately protected from dust. The preparation was then ready to use and it should be kept in a stoppered bottle.

2.3.3 APPARATUS

In the experiment to determine the stability constant, murexide was taken in a 250 mL beaker and $\text{Ni}(\text{NO}_3)_2$ solution was added from a 2.00 mL micro litre burette

(Roger Gilmont, Great Neck, NY). After the addition of ammonia pH measurement was carried out with a Fisher pH meter, Accumet model 320.

A schematic diagram of the titration system is shown in Figure 2.5. The solution in the beaker was constantly stirred by a magnetic stirrer (Fisher economy magnetic stirrer, Catalogue number 14-511-1A) and the solution was pumped by a peristaltic pump operated through tygon pump tubing (2.06 mm id) to a diode array spectrophotometer model no. HP 8452A by an HP 89052B. There were two lines of teflon connecting tubing of 0.5 mm internal diameter for the circulation of solution into and out of the spectrophotometer. The HP 8452A spectrophotometer is equipped with 80 μ L flow cell (HP part no 0100-1225). The resulting spectrum is displayed by HP 89532A MS-DOS UV-Visible General Scanning Software.

2.3.4 STABILITY OF MUREXIDE WITH TIME

Aqueous solutions of murexide are unstable [63]. Normally it is better to prepare a mixture of the indicator with potassium nitrate by grinding 0.1 g of indicator with 10 g of KNO_3 as was done here rather than using an indicator stock solution. When murexide was added to the solution at pH 11.8, it was found that the colour faded after a short time. The stability of murexide in alkali [64], acid [65,66] and in different solvents [67] have been well studied. To see how the absorbance of murexide changes with time at pH 11.8, a solution of murexide was prepared by dissolving 8-10 mg of indicator mixture in 45 mL

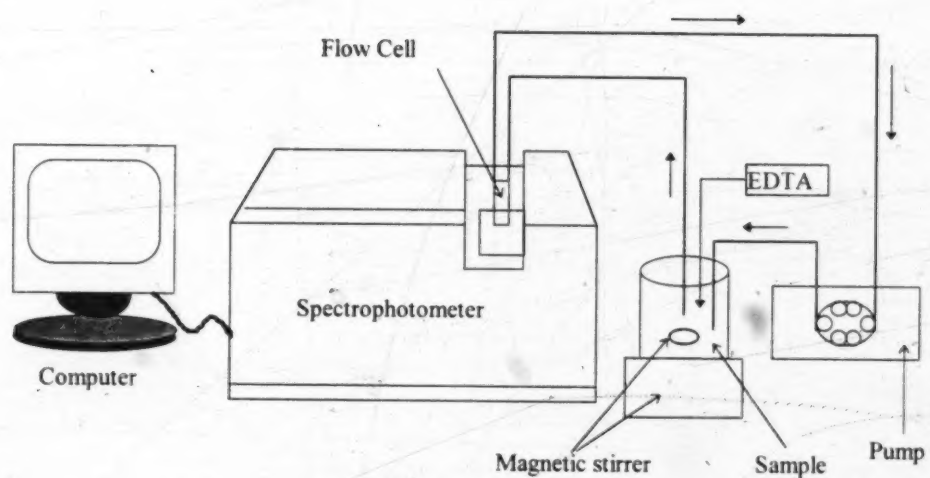


Figure 2.5 : A schematic representation of titration system.

nanopure water and the pH was adjusted to 11.8 by adding 5 mL of concentrated ammonia.

2.3.5 PROCEDURE TO FIND MOLAR ABSORPTIVITIES

To determine the molar absorptivity of murexide, $\epsilon_{550\text{nm}, \text{H}_2\text{In}^{-3}}$, 7-10 mg of accurately weighed indicator mixture was dissolved in a small amount of nanopure water in a beaker. Then, 5 mL of concentrated ammonia (14.5M) was added through a graduate cylinder. Then 45 mL of nanopure water was added using 20 mL and 5 mL pipette. The final volume of solution was 50 mL. The pH of the solution was ensured to be 11.8. More ammonia was again added, if necessary, to obtain the desired pH value. The solution was constantly stirred using a magnetic stirrer. Absorbance was taken at the wavelength $\lambda = 550 \text{ nm}$. A similar procedure was carried out for different weights of indicator. The concentration of murexide was calculated accounting 0.1 g of murexide was mixed with 10 g of KNO_3 . For a plot of absorbance vs concentration, the slope of the line represented the molar absorptivity of murexide at the selected wavelength. Similarly, the molar absorptivity of murexide was measured at $\lambda = 500 \text{ nm}$. The data for finding ϵ at different wavelength is tabulated in Table B11 and Table B 12 in Appendix B and the plot of absorbance vs concentration is shown in Figure A 4 - A 5 in Appendix A.

A similar procedure was employed to find the molar absorptivity of $\text{K}_2\text{Ni}(\text{CN})_4$ by taking about 50 - 60 mg of accurately weighed solid $\text{K}_2\text{Ni}(\text{CN})_4$ in 45 mL nanopure

water, and adjusting the pH to 11.8 by adding 5 mL of conc. ammonia (14.5M). The absorbance was measured at 400 nm. The data for finding ϵ at different wavelength is tabulated in Table B 13 in Appendix B and the plot of absorbance vs concentration is shown in Figure A 6 in Appendix A.

To find the molar absorptivity of $\text{Ni-H}_2\text{In}^-$ complex at $\lambda = 500$ and 550 nm, a standard solution of $\text{Ni}(\text{NO}_3)_2$ (10^{-4}M) was added in small increments, using a micro pipette, to a 50 mL solution of indicator mixture at pH 11.8 which was prepared as discussed above. The solution was constantly stirred using a magnetic stirrer. Ni^{2+} solution was added until all the murexide was converted to nickel - murexide complex. This saturation was confirmed by the fact that increasing the concentration of nickel did not alter the absorbance value. Assuming all murexide was converted to nickel - murexide complex, the concentration of nickel - murexide complex was same as the initial concentration of murexide, after correcting for the small amount of dilution due to the added $\text{Ni}(\text{NO}_3)_2$ stock solution. Then for a plot of the absorbance vs. concentration of nickel - murexide complex, the slope would give ϵ of nickel - murexide complex, $\text{Ni-H}_2\text{In}^-$ at the wavelength employed. The data for finding ϵ at different wavelength is tabulated in Table B 8 to B 10 in Appendix B and the plot of absorbance vs concentration is shown in Figure A1 - A 3 in Appendix A.

2.3.6 PROCEDURE TO FIND STABILITY CONSTANT

In order to find the stability constant of nickel - murexide complex, the following procedural steps were carried out. A solution of indicator was prepared by accurately weighing 7-10 mg of indicator mixture in 45 mL nanopure water and the pH was adjusted to 11.8 by adding 5 mL of conc. ammonia (14.5M) and the final volume was 50 mL. Nickel nitrate (10^{-4} M) was added so that $[\text{Ni-H}_2\text{In}] < [\text{H}_2\text{In}^{3-}]$. The equilibrium between metal ions and the indicator was determined by monitoring absorbance spectrophotometrically. Since the work was done at pH 11.8, the main free murexide species was H_2In^{3-} .

The absorbance at 400 nm will give the concentration of the nickel - murexide complex since murexide has no absorbance at this wavelength. The absorbance at 550 nm was the sum of the absorbances due to the murexide and nickel-murexide complex. The stability constant was then obtained using equations (2.9), (2.11) and (2.12) that are discussed in Sec.2.2.4.

2.4 RESULTS AND DISCUSSION

2.4.1 STABILITY OF MUREXIDE WITH TIME

Murexide had a peak at 550 nm at pH 11.8. Absorbance of murexide with time at the wavelength 550 nm was monitored and a graph of absorbance vs time is shown in Figure 2.6 and the data are shown in Table B1 in the Appendix B. It was found that murexide was fairly stable up to 25 minutes and after 30 minutes it was decomposing more rapidly. At 25 minutes decrease in absorbance was only 7% and there was a 20% decrease in absorbance after 45 minutes. Therefore, the titration must be completed within 30 minutes.

2.4.2 EFFECT OF ABSORBANCE OF NICKEL - AMMINE COMPLEX AT THE WAVELENGTH OF INTEREST

Since the purpose was to find the equilibrium constant of the nickel-murexide complex, it was wise to check that no species other than the species of interest absorb at that particular wavelength. Ammonia was added to keep the pH constant and there was a possibility of the formation of nickel - ammine complexes. By adding concentrated ammonia to a Ni^{+2} solution, in the absence of murexide and monitoring at the wavelengths of interest, i.e. at 400-550 nm, it could be determined whether there was any

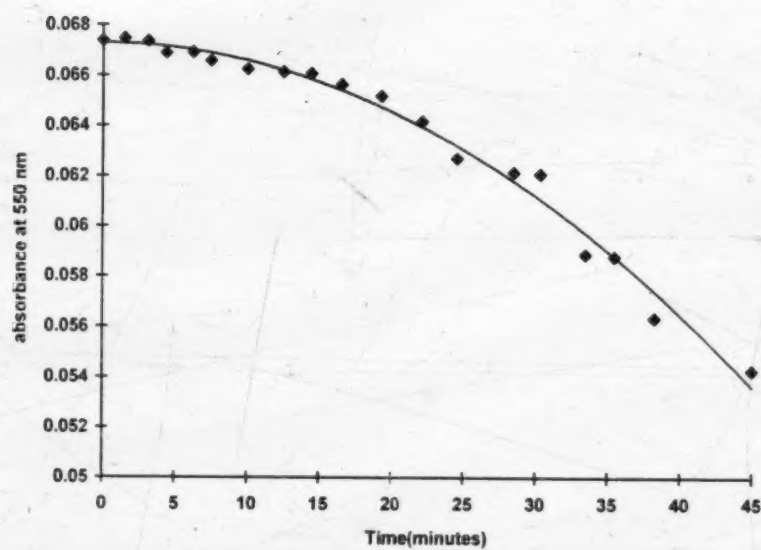


Figure 2.6: Stability of murexide with time (~ 8 mg of indicator mixture in 50 mL nanopure water buffered by 1.4M ammonia at pH 11.8).

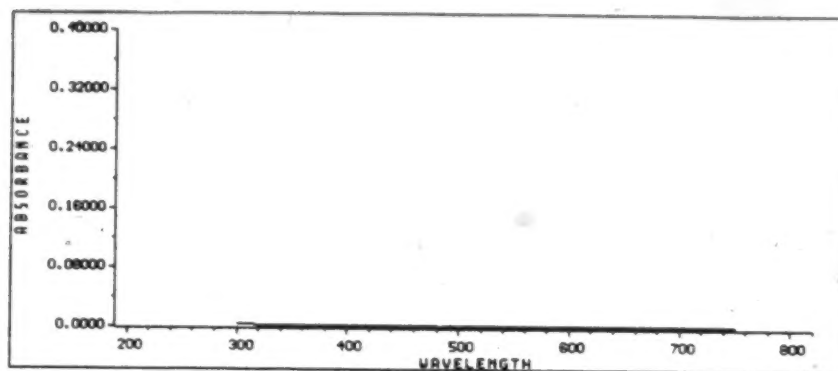
absorbance due to the nickel-ammine species. It was found that at the wavelengths of interest absorbance due to nickel-ammine species was negligible. That is illustrated in Figure 2.7.

2.4.3 FORMATION OF NICKEL HYDROXIDE

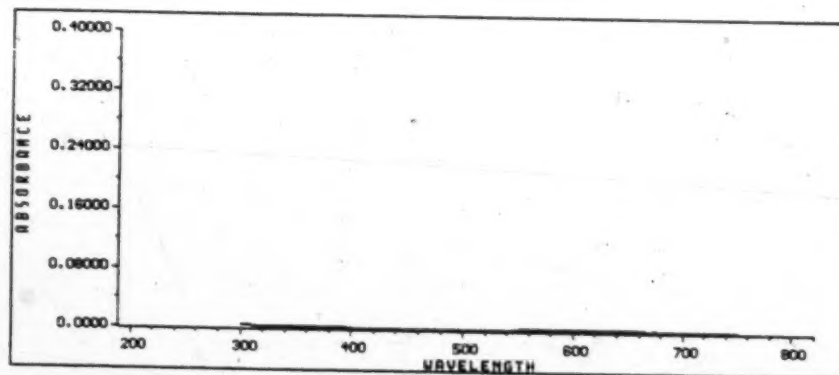
There is a possibility of formation of nickel hydroxide at pH 11.8. Nickel exists in various forms with hydroxide such as $\text{Ni}(\text{OH})^+_{\text{aq}}$ ($\log K_1 = 4.1$), $\text{Ni}(\text{OH})_2$ ($\log K_2 = 8$) and $\text{Ni}(\text{OH})^-_3$ ($\log K_3 = 11$) [53]. At pH 11.8, fraction of free nickel with respect to hydroxide was $\alpha_{\text{Ni,OH}}$ and was equal to 4×10^{-5} . This could be neglected when it was compared with the fraction of free nickel with respect to ammonia at the same pH, $\alpha_{\text{Ni,NH}_3}$, which was 3.48×10^{-10} .

2.4.4 RELEVANCE OF FINDING THE EQUILIBRIUM CONSTANT OF NICKEL - MUREXIDE AT pH 11.8

Ag(I) was determined indirectly by adding potassium tetracyanonickelate to a Ag(I) solution containing ammonia as buffer to make the pH 11.8 and the liberated nickel was titrated spectrophotometrically vs EDTA using murexide as indicator. When a sample solution containing a known concentration of Ag(I) and excess $[\text{Ni}(\text{CN})_4]^{2-}$ was



(A)



(B)

Figure 2.7: (A) Spectrum of $\text{Ni}(\text{NO}_3)_2$ (10^{-4} M Ni^{+2} solution in nanopure water;

(B) Spectrum of $\text{Ni}(\text{NO}_3)_2$ (10^{-4} M Ni^{+2} buffered by 1.4M ammonia; pH 11.8).

titrated against EDTA, it was found that the amount of titrant consumed was greater than the amount of Ag(I) present. Hence it was proved that more Ni^{+2} is liberated from the cyanide complex than the stoichiometric quantity of Ag(I).

In order to account for the extra nickel that was liberated from $[\text{Ni}(\text{CN})_4]^{-2}$, a blank titration was necessary. To run a blank, the solution must contain everything except the analyte, silver. Equation (2.8) accounts the formation of nickel from the cyanide complex in the presence of ammonia and murexide. The constant given in the literature, $\log K = 11.3$, was a conditional constant [50, 51] and the conditions were not given. Hence to solve equation (2.9), the equilibrium constant of nickel and murexide at pH 11.8 has to be determined. The equilibrium constant of nickel with murexide was determined by monitoring the equilibrium concentrations of murexide and nickel murexide. They could be easily found photometrically by using their molar absorptivities (equations 2.11 and 2.12) as discussed in Section 2.2.2. A list of molar absorptivities is tabulated in Table 2.1. A wavelength of 400 nm was chosen to find the concentration of nickel - murexide complex since free murexide has no absorbance at that wavelength, as shown in the table. Above 400 nm both free murexide and nickel - murexide complex absorb. The wavelength of 550 nm was chosen to solve the equation for concentration of free murexide since murexide has an absorbance maximum at that wavelength at pH 11.8.

Equilibrium concentrations of free nickel (from equation 2.10), free murexide and nickel - murexide complex are shown in Table 2.2. An average value of $4.3 \times 10^{15} \text{ M}^{-1} \pm 4 \times 10^{14} \text{ M}^{-1}$ was obtained for the equilibrium constant with a relative standard

deviation of 9.0%. This might be due to the errors associated with reagents volume measurements. The buffer ammonia, was added from a graduate cylinder. The percentage error in a volume of 5.0 mL ammonia added was 2.0%. $\text{Ni}(\text{NO}_3)_2$ was added from a 2.00 mL micro burette and the percentage error associated with 2.00 μL volume was 0.1%. Accounting these errors, the standard deviation that was determined for the value of equilibrium constant was reasonable.

Species that absorb light	Molar absorptivity at Wavelength at 400 nm $M^{-1} cm^{-1}$	Molar absorptivity at Wavelength at 550 nm $M^{-1} cm^{-1}$
$Ni-H_2In^{-}$	4.9×10^3	1.4×10^3
H_2In^{-3}	no absorbance	9.3×10^3

Table 2.1: Molar absorptivities of free murexide and nickel - murexide complex at pH 11.8.

Conc. of $\text{Ni}(\text{NO}_3)_2$ M	Absorbance at 400 nm	Conc. of $\text{Ni-H}_2\text{In}^-$ M	Absorbance at 550 nm	Conc. of H_2In^{3-} M	$[\text{Ni}^{+2}]$ M	$K_{\text{Ni-H}_2\text{In}}$ M^{-1}
2.37×10^{-6}	0.009 ₅	1.9×10^{-6}	0.035 ₁	2.8×10^{-6}	1.5×10^{-16}	4.6×10^{15}
4.74×10^{-6}	0.041 ₆	3.0×10^{-6}	0.026 ₇	1.2×10^{-6}	6.1×10^{-16}	3.9×10^{15}
2.37×10^{-6}	0.010 ₉	3.0×10^{-6}	0.115 ₂	8.8×10^{-6}	5.4×10^{-17}	4.7×10^{15}
4.74×10^{-6}	0.021	4.3×10^{-6}	0.092	6.6×10^{-6}	1.6×10^{-16}	4.0×10^{15}

$$\text{Average } K_{\text{Ni-H}_2\text{In}} = 4.3 \times 10^{15}$$

Table 2.2: Equilibrium concentration of free murexide, nickel - murexide complex, free nickel and stability constant of nickel- murexide complex in 1.4M NH_3 as buffer; pH = 11.8.

CHAPTER 3

BLANK TITRATION

3.1 INTRODUCTION

It was observed that a peak was formed at 442 nm when murexide was added prior to the addition of Ag(I) to an ammoniacal solution of tetracyanonickelate. Both tetracyanonickelate and murexide had little absorbance at that wavelength. Nickel-murexide complex had a peak at 442 nm, suggesting that the metal-indicator complex was formed. Also in the presence of ammonia there was a possibility of formation of nickel-ammine complexes.

The spectrophotometric titration of milligram quantities of silver with EDTA by Gedansky and Gordon [22], was based on differential null point method. According to them the colorimeter was adjusted to read zero absorbance for a solution containing potassium tetracyanonickelate and murexide prior to the addition of Ag(I). Nickel was released upon addition of Ag(I). The titration was then performed with EDTA and absorbance was taken at 442 nm. In a plot of volume of titrant vs absorbance, the intersection of titration curve at the zero absorbance base line was taken as the end point.

In the present work that technique was modified by eliminating the initial adjustment to zero absorbance and selecting the wavelength 550 nm where free murexide

has an absorbance maximum. The blank correction can be calculated by knowing the concentration of tetracyanonickelate added. The accuracy of the blank correction was verified by performing a blank titration. An ammoniacal solution of tetracyanonickelate at pH 11.8 was chosen as the blank solution and it was titrated spectrophotometrically against EDTA using murexide as indicator.

3.2 THEORY

The equilibria involved in a solution containing potassium tetracyano nickelate, ammonia and murexide were discussed in Chapter 2, Section 2.2. The concentration of nickel that is not bound to cyanide in the presence of ammonia and murexide, i.e. blank correction, $C_{\text{Ni, blank}}$ is represented as follows,

$$C_{\text{Ni, blank}} = [\text{Ni}^{2+}] + \beta_1[\text{NH}_3][\text{Ni}^{2+}] + \beta_2[\text{NH}_3]^2[\text{Ni}^{2+}] + \beta_3[\text{NH}_3]^3[\text{Ni}^{2+}] + \beta_4[\text{NH}_3]^4[\text{Ni}^{2+}] + \beta_5[\text{NH}_3]^5[\text{Ni}^{2+}] + \beta_6[\text{NH}_3]^6[\text{Ni}^{2+}] + K_{\text{Ni-H}_2\text{In}}[\text{H}_2\text{In}^{3-}][\text{Ni}^{2+}] \dots (3.1)$$

Since each Ni^{2+} corresponds to 4 cyanide ions,

$$4 C_{\text{Ni, blank}} = C_{\text{CN}^-} \dots (3.2)$$

At pH = 11.8, $\alpha_{\text{CN}^-} = 0.998$, so that $[\text{CN}^-] = C_{\text{CN}^-}$. Therefore equation (3.1) becomes

$$[\text{CN}^-] = 4[\text{Ni}^{2+}] \{ 1 + \beta_1[\text{NH}_3] + \beta_2[\text{NH}_3]^2 + \beta_3[\text{NH}_3]^3 + \beta_4[\text{NH}_3]^4 + \beta_5[\text{NH}_3]^5 + \beta_6[\text{NH}_3]^6 + K_{\text{Ni-H}_2\text{In}}[\text{H}_2\text{In}^{3-}] \} \dots\dots\dots (3.3)$$

At pH = 11.8, $\alpha_{\text{NH}_3} = 0.995$, C_{NH_3} = Total concentration of ammonia = 1.45.

Therefore $[\text{NH}_3] = \alpha_{\text{NH}_3} \cdot C_{\text{NH}_3} = 1.44$. Here the approximation is that concentration of

free buffer was equal to concentration of total buffer since concentration of buffer (1.445M) $\gg$ concentration of metal (10^{-4}M).

Substituting the values of β 's and concentration of ammonia:

$$\beta_1[\text{NH}_3] + \beta_2[\text{NH}_3]^2 + \beta_3[\text{NH}_3]^3 + \beta_4[\text{NH}_3]^4 + \beta_5[\text{NH}_3]^5 + \beta_6[\text{NH}_3]^6 = 2.87 \times 10^9 \dots\dots\dots (3.4)$$

Assuming that the concentration of nickel- murexide complex is negligible compared to the concentration of $\text{K}_2\text{Ni}(\text{CN})_4$ that is not dissociated: $C_{\text{Ni, Total}} = [\text{Ni}(\text{CN})_4^{2-}]$

From equation (2.1),

$$[\text{Ni}^{2+}] = \frac{C_{\text{Ni, Total}}}{[\text{CN}^-]^4} \times 1.31 \times 10^{-31} \dots\dots\dots (3.5)$$

Substituting equations (3.4) and (3.5) in equation (3.3),

$$[\text{CN}^-]^5 = 4 \times C_{\text{Ni, Total}} \times 1.31 \times 10^{-31} \{ 1 + 2.87 \times 10^9 + 4.3 \times 10^{15} [\text{H}_2\text{In}^{3-}] \} \dots\dots\dots (3.6)$$

The value of $[\text{H}_2\text{In}^{3-}]$ for using in equation (3.5) is obtained by simultaneous spectrophotometric analysis at $\lambda = 500 \text{ nm}$ and $\lambda = 550 \text{ nm}$, because $\text{K}_2\text{Ni}(\text{CN})_4$ has a small absorbance at 400 nm and no absorbance above 450 nm.

$$A_{500} = \{(\epsilon_{\text{Ni-H}_2\text{In}})_{500} \times [\text{Ni-H}_2\text{In}] \times b\} + \{(\epsilon_{\text{H}_2\text{In}})_{500} \times [\text{H}_2\text{In}^{3-}] \times b\} \dots (3.7)$$

$$A_{550} = \{(\epsilon_{\text{Ni-H}_2\text{In}})_{550} \times [\text{Ni-H}_2\text{In}] \times b\} + \{(\epsilon_{\text{H}_2\text{In}})_{550} \times [\text{H}_2\text{In}^{3-}] \times b\} \dots (3.8)$$

Using equations (3.7) and (3.8), concentrations of nickel-murexide complex and free murexide can be calculated. Then substituting the concentration of free murexide in equation (3.6), the concentration of free cyanide can be determined. Therefore the concentration of nickel that was not bound to the cyanide complex could be calculated using equation (3.2). This was the concentration of all nickel species that was titrated by EDTA. It includes the species free Ni^{+2} , Ni-ammine complexes and $\text{Ni-H}_2\text{In}^{3-}$. Experimentally the concentration of nickel that is not bound to the cyanide complex could be calculated knowing the volume and molarity of EDTA.

$$C_{\text{Ni, blank}} = \frac{\text{Vol}_{\text{EDTA}} \times M_{\text{EDTA}}}{\text{Volume of sample solution}} \quad (3.9)$$

3.3 EXPERIMENTAL

3.3.1 PROCEDURE FOR BLANK TITRATION

An accurately weighed amount of 25 - 30 mg of $\text{K}_2\text{Ni}(\text{CN})_4$ was dissolved in nanopure water in a beaker. Ammonia was used as buffer, and for that purpose 5 mL of conc. ammonia was added and followed by 45 mL of nanopure water added by 20 and

5 mL pipettes. The concentration of buffer in the final solution was 1.4M. The solution was constantly stirred using a magnetic stirrer. Next, 7-10 mg of indicator mixture was added and the absorbance was measured at wavelengths 500 and 550 nm. Small increments of 4.88×10^{-3} M EDTA were then added from a micro burette. The tip of the tube should be well above the sample solution to avoid diffusion of titrant to the solution. A time of 30-40 seconds was allowed for complete mixing and equilibrium after each addition of the titrant. After the end point there was no appreciable change in absorbance. A plot of absorbance vs volume of titrant is shown in Fig 3.1. and the experimental data are tabulated in Table B 2 in Appendix B.

3.4 RESULTS AND DISCUSSION

During the blank titration, absorbance at 550 nm was observed, because free murexide absorbs at that wavelength. The end point in a blank titration was obtained by plotting absorbance vs volume of the titrant EDTA in milliliters. There was a curvature in the vicinity of the end point. Hence the end point was obtained by the intersection of the least squares lines of the two linear parts of the titration curve as shown in Figure 3.1. Points on the steep part of the curve were selected to draw one straight line portion. Selection of points to draw a straight line was governed by the fact that those points would give the best value for the correlation coefficient.

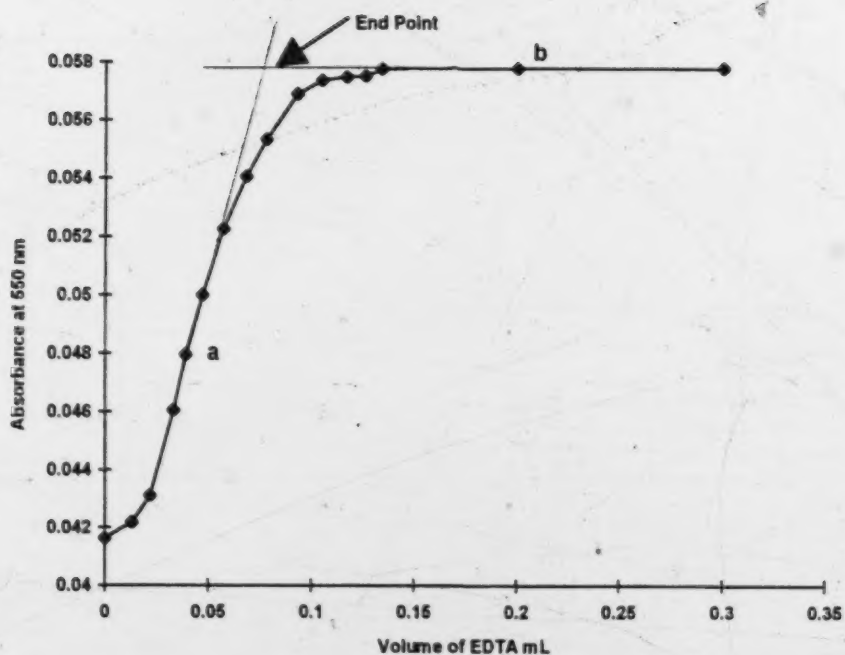


Figure 3.1: A typical blank titration curve: Sample solution contains $5 \times 10^{-3} \text{M}$,

$[\text{Ni}(\text{CN})_4]^{-2}$ and $\sim 8 \text{ mg}$ murexide, buffered by 1.4M ammonia at $\text{pH } 11.8$.

The titrant was $4.88 \times 10^{-3} \text{M}$ EDTA. Volume of EDTA used at the end point was 0.079 mL .

The shape of the graph obtained in Figure 3.1 shows that there is negligible free nickel (i.e. Ni^{+2} hydrated). Otherwise there would be a part in the graph where there is zero slope or only a small one during the initial addition of EDTA. An increase in absorbance was observed due to the murexide released from nickel-murexide complex by the EDTA (part a). When EDTA consumed all nickel from nickel-murexide complex and nickel ammine complexes, no change in absorbance was observed (part b). The end point was determined by extrapolating two straight lines in the region 'a' and 'b' and the point of intersection was taken as the end point.

Molar absorptivities of $\text{K}_2\text{Ni}(\text{CN})_4$, Ni-Murexide complex and free murexide at 400 nm, 500 nm and 550 nm are given in Table 3.1. The procedure to find the molar absorptivity at a particular wavelength is discussed briefly in Chapter 2, Section 2.3.5. Since there is an appreciable difference between the molar absorptivity of nickel murexide complex and free murexide at wavelengths 500 and 550 nm as shown in table 3.1, it is possible to calculate the concentration of two forms of the indicator by monitoring the absorbance at 500 nm and 550 nm before the addition of EDTA. Potassium tetracyanonickelate has a small absorbance below 500 nm. Since $\text{K}_2\text{Ni}(\text{CN})_4$ absorbs at 400 nm, this wavelength cannot be used for the determination of the concentration of Ni-Murexide complex. Therefore simultaneous spectrophotometric analysis at 500 and 550 nm using equations (3.7) and (3.8) gives the equilibrium concentration of Ni-Murexide complex and free murexide respectively. They are tabulated in Table 3.2. There is a substantial difference in molar absorptivity between free murexide and its complexed form at 500 nm and 550 nm as shown in Table 3.1.

$\text{K}_2\text{Ni}(\text{CN})_4$ and murexide were added in solid form. Therefore their concentration was different in each experiment. Equilibrium concentration of $[\text{Ni}(\text{CN})_4]^{2-}$ was the same as initial concentration, assuming its concentration was in excess when compared with the sum of concentration of both nickel-ammine complexes and nickel-murexide complex. The concentration of nickel that was not bound to the cyanide was determined theoretically using equations (3.2) and (3.6). It was determined experimentally using the relationship, 1 mole EDTA $\equiv$ 1 mole Ni^{+2} (equation 3.9). Table 3.2 shows that the experimental results and the theoretical are in good agreement.

The concentration of EDTA titrant was fairly high to minimize the dilution effect and the pH should be kept within 11.2-11.8 range. Nickel was slowly released from murexide complex therefore the titration was carried out slowly towards the end point. At the same time all the experiments should be carried out within 30 minutes since murexide has a faster rate of decomposition in alkaline medium. Otherwise the portion of the graph after the end point would bend more towards the volume axis due to the decomposition of the indicator.

Species that absorb light	Molar absorptivity at wavelength 400 nm $M^{-1}cm^{-1}$	Molar absorptivity at wavelength 500 nm $M^{-1}cm^{-1}$	Molar absorptivity at wavelength 550 nm $M^{-1}cm^{-1}$
$K_2[Ni(CN)_4]$	6.0	no absorbance	no absorbance
$Ni - H_2In^{-}$	4.9×10^3	12×10^3	1.4×10^3
H_2In^{-3}	no absorbance	9.4×10^3	9.3×10^3

Table 3.1: Molar absorptivities of $K_2[Ni(CN)_4]$, $Ni-H_2In^{-}$ complex and free murexide buffered by 1.45M ammonia at pH 11.8

Data No.	Absorbance at 500nm	Absorbance at 550nm	$[\text{Ni}(\text{CN})_4]^{2-}$ $\text{M} \times 10^{-3}$	$[\text{Ni-H}_2\text{In}]$ $\text{M} \times 10^{-6}$	$[\text{H}_2\text{In}^{3-}]$ $\text{M} \times 10^{-6}$	$C_{\text{Ni, blank experimentally}}$ $\text{M} (\times 10^{-6})$	$C_{\text{Ni, blank theoretically}}$ $\text{M} (\times 10^{-6})$
1	0.054 ₁	0.041 ₆	2.37	1.1	4.3	7.7	7.6
2	0.045 ₄	0.030 ₂	5.06	1.4	3.0	8.4	8.4
3	0.073 ₀	0.058 ₂	5.14	1.3	6.0	9.5	9.4

Table 3.2 : Comparison of concentration of nickel that was not bound to cyanide (i.e. the blank value) which was found experimentally with theoretical blank value. Theoretical value was obtained by using equations (3.2) and (3.6) and experimental value was obtained by using equation (3.9).

CHAPTER 4

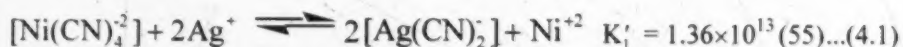
INDIRECT TITRATION OF SILVER WITH EDTA USING A VISUAL END POINT

4.1 INTRODUCTION

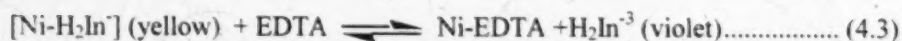
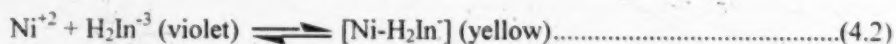
The stability of Ag-EDTA complex ($\log K_{\text{Ag-EDTA}} = 7.2$) [4] is too small to permit a direct titration with a complex-forming indicator. Another route to an indirect titration is through an exchange reaction with tetracyanonickelate, $[\text{Ni}(\text{CN})_4]^{-2}$ whereby an equivalent amount of nickel was set free by Ag(I) for titration with EDTA using murexide [15-20] as indicator. Since silver has a higher affinity for cyanide ion than nickel, the ionic exchange reaction proceeds almost completely. The visual end point was determined by the colour change of murexide indicator from yellow to purple-violet. The reaction was carried out in the presence of ammonia-ammonium chloride buffer at pH 10 [16,18]. The visual titration was carried out at the pH 10 instead of pH 11.8 which was used in the spectrophotometric titrations. To see whether the above reaction would take place in the presence of a water insoluble silver halide, the same experiment was carried out in the presence of 0.15M sodium chloride.

4.2 THEORY

When a solution of Ag(I) was added to ammoniacal solution of potassium tetracyanonickelate(II), a quantitative amount of nickel was released which can be titrated with EDTA using murexide as indicator. The reactions that take place can be represented as follows.



Murexide above pH 10 can be represented as H_2In^{3-}



According to equation (4.1), two silver ions are equivalent to one released nickel ion. Therefore 1 mL 0.01M EDTA = 2.1576 mg of silver. The end point was determined by the colour change from yellow to violet. The overall stability constant of the complex ion $[\text{Ni}(\text{CN})_4]^{2-}$ is 7.6×10^{30} [52,53,55] and that of $[\text{Ag}(\text{CN})_2]$ is 10^{21} [55,68,69] which implies that the equation (4.1) would go nearly completely to the right.

Experimentally an unknown concentration of Ag(I) was determined using the following equation,

$$[\text{Ag}^+] = \frac{\text{Vol}_{\text{EDTA}} \times M_{\text{EDTA}} \times 2}{\text{Volume of silver solution}} \dots\dots\dots (4.4)$$

4.3 EXPERIMENTAL

4.3.1 REAGENTS AND CHEMICALS

Silver nitrate was purchased from Caledon, NaCl was purchased from BDH chemicals and ammonium chloride was Baker Analysed. All solutions were prepared in nanopure water. The 0.01M EDTA was prepared by dissolving 3.7224 g of $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ per litre of solution. The prepared solution of EDTA was then stored in a polythene bottle. The EDTA was standardised using a known quantity of silver. Silver was used for standardisation to eliminate all possible errors associated with the detection of end point. Molarity of EDTA that was used for the visual titration was 0.00503. This was prepared from 0.01M stock solution.

To prepare silver nitrate solution, some finely powdered analytical grade silver nitrate was dried at 120°C for two hours and was allowed to cool in a covered vessel in a desiccator. Then exactly 8.494 g was dissolved in nanopure water and made up to 500.0 mL in a volumetric flask. The concentration of Ag^+ in the final solution was 0.1000M. More dilute solution was prepared from the stock solution. Solutions of silver nitrate were protected from light and were stored in amber-coloured glass bottle.

Buffer of pH 10, was made by dissolving 70 g of ammonium chloride in 570 mL ammonia and was diluted with nano pure water to 1L. The solution was then stored in a plastic container. To conduct a titration in the presence of chloride ion, a definite amount

of 1M NaCl was pipetted into the sample solution so that concentration of chloride was 0.15M.

4.3.2 EXPERIMENTAL PROCEDURE

Accurately weighed potassium tetracyanonickelate (0.2-0.3 g) was dissolved in small amount of nanopure water in a 250 mL conical flask. About 10 mL of ammonia-ammonium chloride buffer of pH 10 was added from a graduate cylinder. Then a few mg of murexide indicator mixture was added using a spatula and 20 mL of 0.01M silver nitrate solution was pipetted into the flask. Then nanopure water was added from a 50.0 mL graduate cylinder to make the final volume 70.0 ± 0.6 mL. The titrant EDTA (0.00503M) was taken in a 50 mL burette and titrated until the colour of the solution in the conical flask changes from yellow to purple-violet. The end point was very sharp. A few drops before the end point the colour changes to an orange tint. The final change to permanent violet was easily seen within a drop or fraction of a drop of EDTA solution. The complexing of nickel was somewhat slow, therefore EDTA was added slowly as it approaches the end point. The titration was done at room temperature.

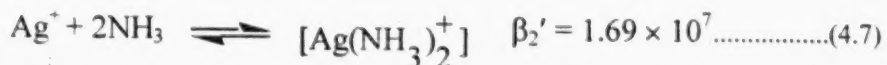
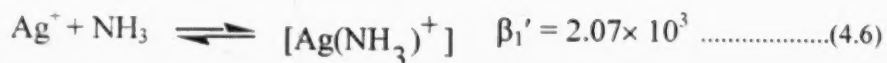
The above procedure was repeated in the presence of chloride ion by adding 10.5 mL of 1M sodium chloride to the sample solution. The concentration of chloride in the 70 mL sample solution was 0.15M.

4.4 RESULTS AND DISCUSSION

The obtained results of the titration are shown in Table 4.1 and 4.2. The titration results given in Table 4.1 yield a mean of 19.91 mL and a standard deviation of 0.01 mL and a relative standard deviation of 0.07%. In the presence of excess chloride ion, all of the silver halide precipitate formed has dissolved into the solution and obtained a mean of 19.92 mL and a standard deviation of 0.02 mL and a relative standard deviation of 0.1%. Potassium tetracyanonickelate complex was added in solid form hence its amount varies among the titrations. There is a danger of forming sparingly soluble nickel tetracyanonickelate(II) by the following reaction [54],



To avoid this precipitation, sufficient ammonia was added to transform the cyanide-free nickel into its ammine complexes (equations 2.2 - 2.7). Furthermore, any Ag(I) that was not bound to cyanide will also occur as the ammine complex $[\text{Ag}(\text{NH}_3)_2]^+$. These reactions can be represented as follows.



Using equation (3.4), the total concentration of nickel that is not bound to cyanide, C_{Ni} was calculated. The total concentration of Ag(I) that is not bound to cyanide C_{Ag} was calculated using equations (4.6) and (4.7). Thus:

$$C_{Ni} = \sum_{j=0}^6 [Ni(NH_3)_j] = 2.9 \times 10^9 [Ni^{+2}] \dots\dots\dots(4.8)$$

$$C_{Ag} = \sum_{j=0}^2 [Ag(NH_3)_j] = 10^7 [Ag^+] \dots\dots\dots(4.9)$$

Substituting C_{Ag} and C_{Ni} in equation (4.1), the following value was obtained for the actual equilibrium at an ammonia concentration of about 1M ,

$$\frac{C_{Ni} [Ag(CN)_2]^{-2}}{C_{Ag}^2 [Ni(CN)_4]} = 3.9 \times 10^8 \dots\dots\dots(4.10)$$

Using the first set of experimental data in Table 4.1, equilibrium concentration of species in equation (4.1) are :

$$[Ni(CN)_4]^{-2} = \text{total concentration of nickel cyanide complex} - C_{Ni} = 1.77 \times 10^{-2}$$

$$(\pm 0.02 \times 10^{-2})M, [Ag(CN)_2]^{-} = 2.9 \times 10^{-3} (\pm 0.2 \times 10^{-3})M \text{ and}$$

$$C_{\text{Ni}} = \frac{\text{Ag}(\text{CN})_2}{2} = 1.4 \times 10^{-3} (\pm 0.2 \times 10^{-3}) \text{ M} \text{ assuming reaction (4.1) goes completely to}$$

the right. Therefore C_{Ag} can be calculated using equation (4.10). Hence in the presence

of excess tetracyanonickelate the value of C_{Ag} drops to about $4.1 \times 10^{-8} \text{ M}$ and the

concentration of free silver ions, i.e. $[\text{Ag}^+]$, to about 4.1×10^{-15} (using equation 4.9), and

this was sufficiently low to bring even the very sparingly soluble AgI into solution.

Hence this experiment proves that the exchange also takes place quantitatively with sparingly soluble silver salts, so that silver halide precipitates can be titrated. Thus titration of silver makes all those anions that can be precipitated by Ag^+ accessible to complexometric titration. Thus this titration can be carried out to measure all silver(I) species, even silver halides.

Weight of $K_2Ni(CN)_4$ (g)	Volume of $AgNO_3$ (0.01001M) pipetted out (mL)	Volume of EDTA calculated theoretically (mL)	Volume of EDTA used (mL) ± 0.07
0.29872	20.012	19.91	19.90
0.29451	20.012	19.91	19.91
0.29581	20.012	19.91	19.93
0.29762	20.012	19.91	19.90

Average = 19.91
Standard deviation = 0.01

Table 4.1 : Visual titration of 0.01001M silver nitrate buffered by NH_3-NH_4Cl buffer with 0.00503M EDTA

in the absence of chloride at pH 10. Volume of EDTA used at the end point is calculated theoretically using equation (4.5).

Weight of $K_2Ni(CN)_4$ (g)	Volume of $AgNO_3$ (0.01001M) pipetted out (mL)	Volume of EDTA calculated theoretically (mL)	Volume of EDTA used (mL) ± 0.07
0.29633	20.012	19.91	19.91
0.03017	20.012	19.91	19.94
0.29891	20.012	19.91	19.92

Average = 19.92
Standard deviation = 0.02

Table 4.2 : Visual titration of 0.01M silver nitrate buffered by NH_3-NH_4Cl buffer with 0.00503M EDTA in the presence of 0.15M chloride at pH 10. Volume of EDTA used at the end point is calculated theoretically using equation (4.5).

CHAPTER 5

SPECTROPHOTOMETRIC DETERMINATION OF Ag(I)

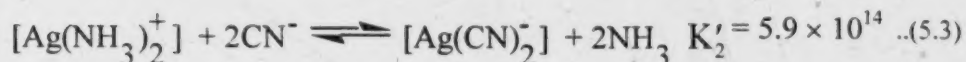
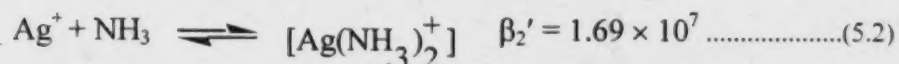
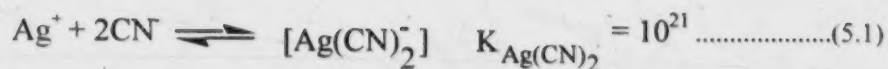
5.1 INTRODUCTION

Indirect determination of Ag(I) using EDTA, as described in Chapter 4, poses difficulty in locating the visual end point when silver was present in low concentrations [22]. The colour change from yellow to violet is gradual, making it difficult to visually locate the exact end point. Gedansky and Gordon extended the method to micro scale determination of silver by a photometric titration technique [22] employing a differential null point method for the detection of end point as discussed in Chapter 2. According to their procedure, the colorimeter was adjusted to read zero absorbance for a solution containing potassium tetracyanonickelate and murexide prior to the addition of Ag(I). Ag(I) solution was then added and the titration was performed with EDTA until the absorbance returned to zero. The absorbance was taken at 400-480 nm. In a plot of volume of titrant vs absorbance, the intersection of titration curve at the zero absorbance base line was taken as the end point. This technique obviates the necessity of determining the blank.

Their procedure was modified to the traditional end point determination by plotting volume of the titrant vs. absorbance as discussed in Chapter 2. The volume of EDTA at the end point was equivalent to the sum of concentration of nickel that was displaced by Ag(I) and the blank. Knowing the blank correction, the concentration of Ag(I) could be measured accurately. Murexide that was unusable in the visual titration because of the sluggish end point was successfully used in the photometric titration. Most metals would interfere with the above method due to the complex formation of metals with murexide or EDTA. The interference was well studied [14,22] and silver can be easily separated from the interfering elements like barium, zinc, copper or iron by precipitation, ion exchange or extraction procedures [1,2].

5.2 THEORY

Ag(I) reacts with ammoniacal nickel cyanide complex to liberate a quantitative amount of nickel. The liberated nickel forms an yellow coloured complex with murexide indicator. The titrant EDTA was added, until no change in absorbance was observed. At this point, all murexide will be free from nickel-murexide complex and the colour changes from yellow to violet. These reactions were represented in equations (4.1) - (4.3). The effects of murexide and ammonia on the dissociation of nickel cyanide complex were discussed in Chapter 2. The other equilibria involved in the sample solution are shown below.



Mass balance for nickel

$$C_{\text{Ni, Total}} = C_{\text{Ni}} + [\text{Ni}(\text{CN})_4]^{2-} \dots\dots\dots(5.4)$$

where $C_{\text{Ni, Total}}$ = Concentration of all species of nickel, C_{Ni} = Concentration of nickel

species that is not bound to cyanide, $[\text{Ni}(\text{CN})_4]^{2-}$ = Concentration of undissociated

cyanide complex. Rearranging equation (5.4), $C_{\text{Ni, Total}} - [\text{Ni}(\text{CN})_4]^{2-} = C_{\text{Ni}}$ = The

concentration of all species of nickel that is titrated with EDTA.

From equations (5.1) and (5.3), it is evident that almost all Ag(I) species will exist

as silver cyanide complex after the reaction with nickel cyanide complex. The

concentration of nickel that is displaced by Ag(I) from the nickel cyanide complex is

$\frac{[\text{Ag}^+]}{2}$, from equation (4.1). Since the blank consumes some EDTA, it is necessary to

account for nickel displaced from the nickel cyanide complex in the presence of blank

alone, as discussed in Chapter 3. Therefore, the concentration of nickel that is not bound

to cyanide will be the sum of concentration of Ag(I) added and the blank correction.

$$C_{\text{Ni}} = \frac{[\text{Ag}^+]}{2} + C_{\text{Ni, blank}} \dots\dots\dots (5.5)$$

where $C_{\text{Ni, blank}}$ is the concentration of nickel that is released from the cyanide complex

in the presence of blank, i.e. the blank correction.

It can be calculated experimentally knowing the volume of EDTA consumed.

$$C_{\text{Ni}} = \frac{\text{Vol}_{\text{EDTA}} \times M_{\text{EDTA}}}{\text{Volume of sample solution}} \dots\dots\dots (5.6)$$

The equation to determine the blank correction as theoretically derived in Chapter 3

(equation 3.6), is:

$$[\text{CN}^-]^5 = 4[\text{Ni}(\text{CN})_4]^{-2} \times 1.31 \times 10^{-31} \{1 + 2.87 \times 10^9 + 4.3 \times 10^{15} [\text{H}_2\text{In}^{3-}]\} \dots\dots\dots (5.7)$$

But when the concentration of Ag(I) is much higher than the concentration of murexide,

there will not be any free murexide. Hence we could neglect the last term in equation

(5.7) which lead to

$$[\text{CN}^-]^5 = 4[\text{Ni}(\text{CN})_4]^{-2} \times 1.31 \times 10^{-31} \{1 + 2.87 \times 10^9\} \dots\dots\dots (5.8)$$

where, $[\text{Ni}(\text{CN})_4]^{-2} = C_{\text{Ni, Total}} - C_{\text{Ni}}$

Therefore by rearranging equation (3.2) and combining equations (5.4), (5.6) and (5.8) the

following relationship can be used to predict the blank.

$$C_{\text{Ni, blank}} = \frac{[\text{CN}^-]}{4} \dots\dots\dots (5.9)$$

Then equation (5.5) becomes,

$$C_{\text{Ni}} = \frac{[\text{Ag}^+]}{2} + \frac{[\text{CN}^-]}{4} \dots\dots\dots(5.10)$$

5.2 EXPERIMENTAL

5.2.1 REAGENTS AND CHEMICALS

Potassium tetracyanonickelate(II) was synthesised as discussed in Chapter 2, Section 2.3.2. Murexide was prepared by grinding 0.1 g of indicator with 10 g of KNO_3 and this indicator mixture would be used in all experiments that follow. To prepare 0.01M EDTA, 3.7224 g of disodium salt of EDTA was accurately weighed and dissolved in 1 litre of nanopure water. It was then spectrophotometrically standardised by known quantities of Ag(I) . The solution was stored in polythene bottles. Ag(I) solutions were prepared as discussed in Chapter 4, Section 4.3.1. Concentrated ammonia was added as buffer. For this purpose 5 mL of concentrated ammonia was added in to 45 mL of sample solution so that the concentration of ammonia in the final volume was 1.4M. Silver oxide was purchased from Aesar and 0.15M NaCl was prepared as discussed in Chapter 4.

To prepare sample solutions from silver oxide, 14-17 mg of accurately weighed silver oxide was added in a 500 mL volumetric flask. Silver oxide was weighed in an air-free atmosphere to prevent any formation of silver carbonate. Therefore the vials in which solid silver oxide was weighed must be filled with an inert gas like helium or nitrogen.

Then 0.5-1 g of accurately weighed $K_2Ni(CN)_4$ and a few mL of nanopure water were added to the 500 mL volumetric flask and shake well. Ammonia was then added to make the pH 11.8. Concentration of ammonia in the final volume was 1.4M. Then small quantities of nano pure water were added and shaken well until all the silver oxide was dissolved. It was then made up to 500 mL with nano pure water. A 50 mL portion of this solution was taken for the spectrophotometric titration.

5.3.2 EXPERIMENTAL PROCEDURE

A 30 - 60 mg of accurately weighed potassium tetracyanonickelate(II) was dissolved in small amount of nanopure water in a 250 mL beaker. Then 7.011 mL of 0.001008M $AgNO_3$ was pipetted out using a 7 mL pipette and 5.0 (± 0.1) mL of concentrated ammonia was added to make the pH 11.8. Then 38 mL (± 0.5) of nanopure water was added through a 50 mL graduate cylinder. Concentration of ammonia in the final volume was 1.4M. Murexide indicator mixture (approximately 8 mg) was then added to obtain a golden yellow solution. The solution was continuously stirred using a magnetic stirrer. The titration system was described in Chapter 2, Section 2.3.3.

Small increments of standard EDTA (0.01007M) was added from a 2.00 mL micro burette and titrated photometrically at 550 nm until no change in absorbance was observed. At least one minute was allowed for complete mixing after each addition of EDTA. The procedure was repeated in the presence of 0.15M NaCl to see whether the

result was reproducible in the presence of halide ion and the experiment was repeated using silver oxide instead of silver nitrate. The end point can be obtained by plotting volume of EDTA vs absorbance.

5.4 RESULTS AND DISCUSSION

The spectra of the system containing Ag(I), potassium tetracyanonickelate and murexide at pH 11.8 before adding EDTA (A) and after the end point (B) are shown in Figure 5.1. The absorption peak (A) at wavelength at 442 nm in Figure 5.1 corresponds to the yellow form of the nickel-murexide complex while the peak at 545 nm (B) corresponds to the free murexide after nickel has been removed from nickel-murexide complex by the EDTA. Since potassium tetracyanonickelate has small absorbance at 400-450 nm region, the wavelength at 550 nm was suitable for the following course of the titration.

Figure 5.2 shows a typical titration curve for Ag(I). As can be seen from the curve, during the initial addition of EDTA the free nickel was complexed. In a plot of millilitres versus absorbance this part of the titration curve will have only a slight slope (part a, Figure 5.2). When all of the free metal has been combined with EDTA, the next increments of titrant will begin to remove the nickel from the indicator complex. This step was accompanied by a much larger change in absorbance (part b, Figure 5.2). When all of the nickel was removed from the indicator and nickel-ammine complexes, any

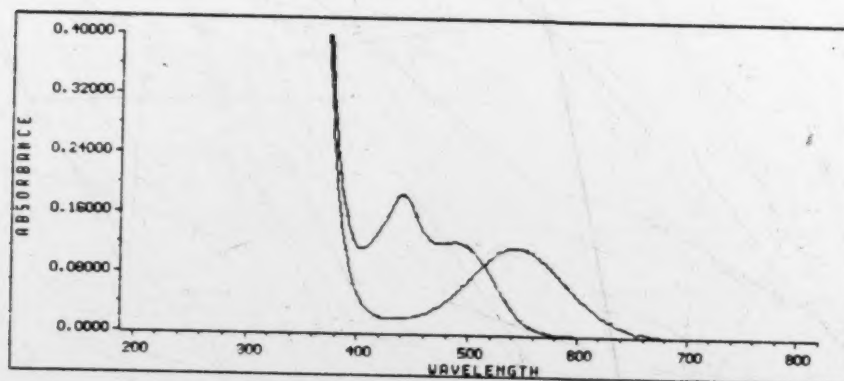


Figure 5.1: Absorption spectra of silver nitrate (0.001008 M)-potassium tetracyanonickelate(II)-murexide and ammonia buffer system at pH 11.8 during titration with 0.01M EDTA

- A Start of titration (no EDTA was added)
- B After the end point (excess EDTA was added)

further addition of EDTA will not change the absorbance, except by dilution (part c, Figure 5.2). A similar type of graph was obtained in the presence of NaCl (Figure 5.3) and with the titration of silver oxide with EDTA (Figure 5.4). The end point was determined by the intersection of the least squares lines of the two linear parts of the titration curve as shown in Figure 5.2. The data of these titrations are tabulated in Table B 3 - Table B 5 in Appendix B.

Tables 5.1 and 5.2 show the result of titration of silver nitrate with EDTA in the absence and in the presence of sodium chloride respectively. Potassium tetracyanonickelate was added in solid form. Therefore its concentration varies among the runs. The blank correction that is shown in Table 5.1 and Table 5.2 is calculated using equation (5.9) and the number of moles of Ag(I) is calculated using equation (5.5) and (5.6) knowing the volume of silver added. An average of 7.062×10^{-6} moles, a standard deviation of 1×10^{-8} moles and a relative standard deviation of 0.1% was obtained for the results in Table 5.1. An average of 7.042×10^{-6} moles, a standard deviation of 1×10^{-8} moles and a relative standard deviation of 0.2% was obtained for the results in Table 5.2.

Using first set of experimental data in Table 5.1, equilibrium concentration of species of the reaction, $[\text{Ni}(\text{CN})_4]^{2-} + 2\text{Ag}^+ \rightleftharpoons 2[\text{Ag}(\text{CN})_2]^- + \text{Ni}^{+2}$ in 50.0 mL are

$$[\text{Ni}(\text{CN})_4]^{2-} = C_{\text{Ni, Total}} - \frac{\text{Vol}_{\text{EDTA}} \times M_{\text{EDTA}}}{\text{Volume of sample solution}} = 2.66 \times 10^{-3} (\pm 0.03 \times 10^{-3})\text{M},$$

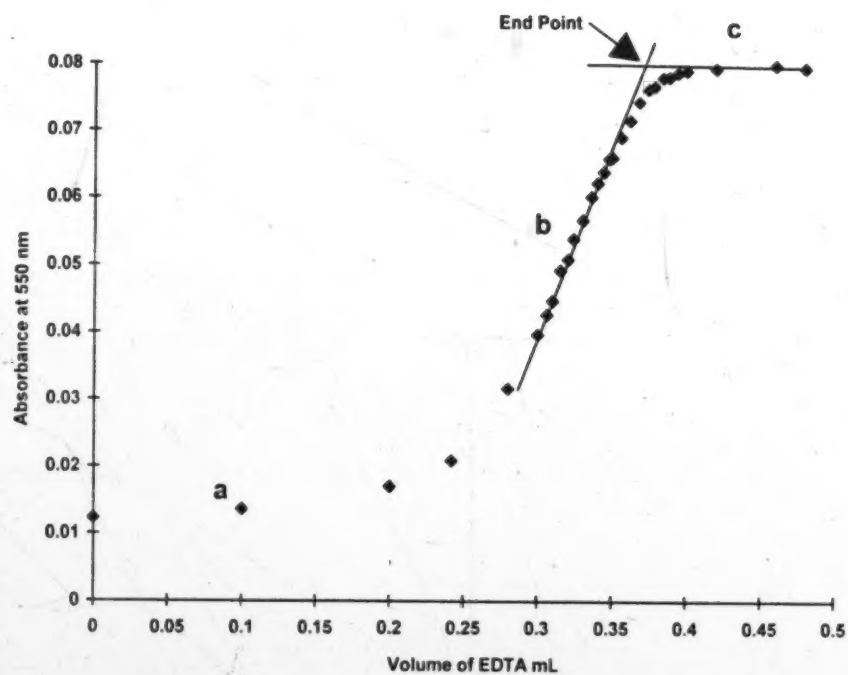


Figure 5.2: Photometric titration of silver nitrate: Sample solution contains 1.41×10^{-4} M silver nitrate, ~ 8 mg of murexide indicator mixture and 2.67×10^{-3} M potassium tetracyanonickelate. 1.4M ammonia was used as buffer to make the pH 11.8. Volume of EDTA used at the end point was 0.375 mL.

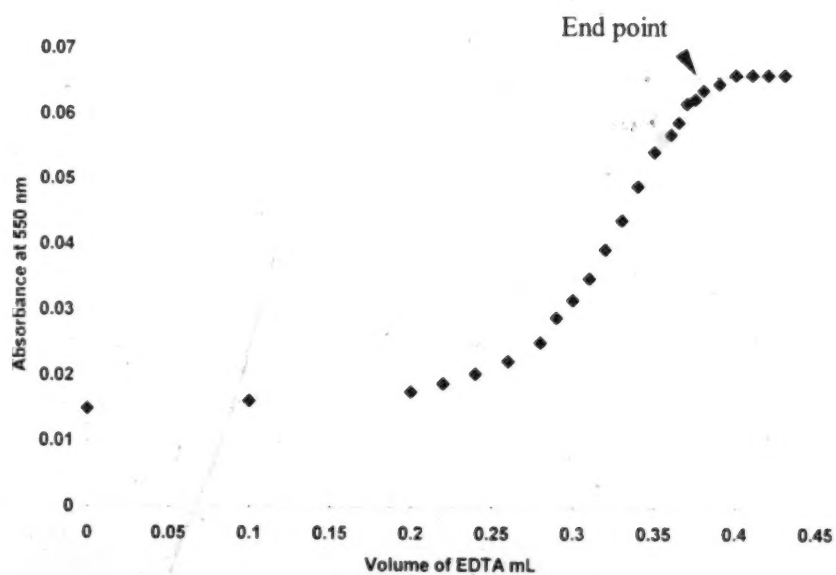


Figure 5.3: Photometric titration of silver nitrate in presence of 0.15M NaCl: Sample solution contains 1.41×10^{-4} M silver nitrate, ~ 8 mg of murexide indicator mixture, 0.15M NaCl and 2.79×10^{-3} M potassium tetracyanonickelate. 1.4M ammonia was used as buffer to make the pH 11.8. Volume of EDTA used at the end point was 0.376 mL.

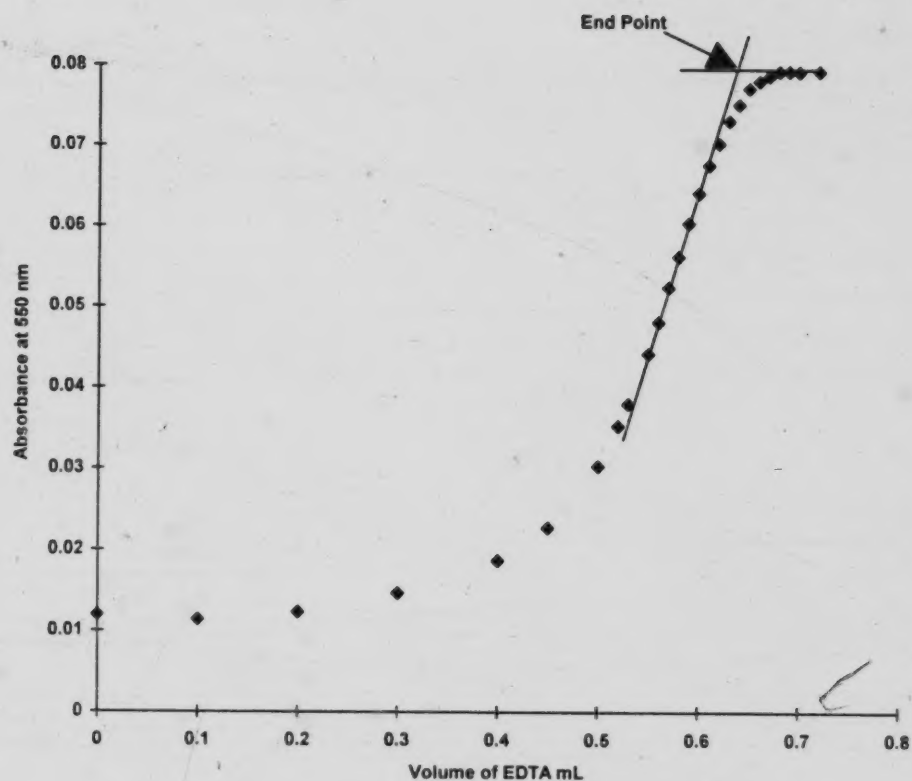


Figure 5.4: Photometric titration of silver oxide: Sample solution contains $2.38 \times 10^{-4}M$ silver oxide, ~ 8 mg of murexide indicator mixture and $9.90 \times 10^{-3}M$ potassium tetracyanonickelate. 1.4M ammonia was used as buffer to make the pH 11.8. Volume of EDTA used at the end point was 0.624 mL.

$[\text{Ag}(\text{CN})_2]^- = 1.4 \times 10^{-4} (\pm 0.1 \times 10^{-4}) \text{M}$ and concentration of nickel that is not bound to cyanide $= 7.6 \times 10^{-5} (\pm 0.1 \times 10^{-5}) \text{M}$ using equation (5.6). The concentration of silver that is not bound to cyanide, C_{Ag} , was calculated using equation (4.10) which is equal to 10^{-9} . Therefore concentration of free silver, including free from ammonia is calculated using equation (4.9) which is equal to 10^{-16} . Thus it proves that all silver halide precipitate formed has dissolved into the solution. Restricting the quantity of concentrated ammonium hydroxide to between 3- 10 mL in the entire titration volume resulted in a pH range from 11.3 to 11.8. When there were large amount of ammonia present the results were not linear with respect to the increasing quantities of silver [22]. This effect have also been observed by Harris and Sweet [70], who found that the end point, in a similar titration of nickel with EDTA, became indistinct.

A blank titration was not necessary in order to account for the blank. The quantity of nickel cyanide complex must be accurately weighed. Knowing the concentration of nickel cyanide added, a blank correction could be made using equation (5.9). This prediction was tested in Chapter 3 and results in Table 3.2 proved that theoretical and experimental results were in good agreement. About 8 mg of murexide was added using a spatula so that the colour of the solution changes to golden yellow after the addition of murexide. The solution must be stirred constantly using a magnetic stirrer and should allow at least one minute for complete mixing of the solution after each addition of

No	Molarity of $K_2Ni(CN)_4$ (M)	Volume of 0.01007M EDTA used (mL) ± 0.001	Blank correction $M \times 10^{-6}$	Volume of EDTA after blank correction (mL)	Number of moles of silver added	Number of moles of silver found
1	0.00267	0.376	5.20	0.350	7.067×10^{-6}	$7.04_9 \times 10^{-6}$
2	0.00274	0.377	5.20	0.351	7.067×10^{-6}	$7.06_9 \times 10^{-6}$
3	0.00255	0.377	5.19	0.351	7.067×10^{-6}	$7.06_9 \times 10^{-6}$
Average = 7.062×10^{-6}						

standard deviation = 1×10^{-8}

Table 5.1: Results of spectrophotometric titration of silver nitrate with 0.01007M EDTA: Sample solution

contains 7.011 mL of 0.001008M $AgNO_3$, $2.74 \times 10^{-3}M$ potassium tetracyanonickelate and murexide, pH was adjusted to 11.8 by 1.4M ammonia. Blank correction was calculated using equation (5.9) and number of moles of silver was determined using equations (5.5) and (5.6).

No	Molarity of $K_2Ni(CN)_4$ (M)	Volume of 0.01007M EDTA used (mL) ± 0.001	Blank correction $M \times 10^{-6}$	Volume of EDTA after blank correction (mL)	Number of moles of silver added	Number of moles of silver found
1	0.00287	0.375	5.28	0.349	7.067×10^{-6}	$7.02_8 \times 10^{-6}$
2	0.00279	0.376	5.18	0.350	7.067×10^{-6}	$7.04_9 \times 10^{-6}$
3	0.00304	0.377	5.34	0.350	7.067×10^{-6}	$7.04_9 \times 10^{-6}$

Average = 7.042×10^{-6}

Standard deviation = 1×10^{-8}

Table 5.2: Results of spectrophotometric titration of silver nitrate with 0.01007M EDTA in the presence of 0.15M NaCl:

Sample solution contains 7.011 mL of 0.001008M $AgNO_3$, $2.87 \times 10^{-3}M$ potassium tetracyanonickelate, 0.15M

NaCl and murexide, pH was adjusted to 11.8 by 1.4M ammonia. Blank correction was calculated using equation (5.9) and number of moles of silver was determined using equations (5.5) and (5.6).

EDTA. The concentration of EDTA must be sufficiently high to eliminate dilution effect.

Ali titrations must be carried out within 30 minutes, otherwise the indicator will decompose and the colour of the solution fades.

CHAPTER 6

SPECTROPHOTOMETRIC TITRATION OF SYNTHETIC MIXTURE OF Ag(0) AND Ag(I) WITH EDTA

6.1 INTRODUCTION

Silver is among the less common but widely distributed elements in the earth's crust. It has been known for long for its broad spectrum of antimicrobial properties. To primitive forms of life, silver is as toxic as the most powerful chemical disinfectant. This oligodynamic activity of silver coupled with its relatively low toxicity to higher forms of life, gives it great potential as a disinfectant. The activity of a specified amount of silver is related to the concentration of silver ions rather than to the chemical or physical nature of the silver. Insoluble compounds of silver or metallic silver can affect micro-organisms by forming minute traces of ionic silver, either through a chemical reaction or through electrolysis [49]. Colloidal silver is used in wound antisepsis and in combination with citrate salts for skin infections. In the past few years its potential for clinical utility has been evaluated. Electrically generated silver ions have been used as adjunctive treatment in the management of chronic osteomyelitis [45]. Most recently a radiolabel adherence procedure provided a quantitative method for evaluating the relative antimicrobial

efficacy of silver-treated catheters [44]. Silver coated materials have been well studied for their antimicrobial activities. The release of silver from silver coating may be in elemental silver, silver oxide or silver chloride. To study the biological action of silver coatings a better understanding of different forms of silver present in the solution is necessary.

The underlying idea for the studies is to determine Ag(I) in the presence of Ag(0). It was proved that Ag(I) in hydrated form, or in a water insoluble silver salt, could be titrated with EDTA as outlined in Chapter 4 and 5, in the Result and Discussion Section. A synthetic mixture of Ag(0) and Ag(I) in ammoniacal tetracyanonickelate at pH 11.8 was prepared and titrated with EDTA. The Ag(0) that was present in the solution would remain in the same oxidation state as long as air is prevented from entering the titration system. To find how Ag(0) behaves in the absence of oxygen, Ag(0) powder was added to an ammoniacal tetracyanonickelate at pH 11.8 and titrated with EDTA using murexide as indicator.

6.2 EXPERIMENTAL

6.2.1 REAGENTS AND CHEMICALS

Metallic silver powder was purchased from Aldrich. Its particle size is in 5-8 μ range. The bottle was always opened in a glove bag filled with nitrogen. The glove bag

was purchased from Cole-Parmer and nitrogen from Proxair. The EDTA titration was done in an air free atmosphere. For that purpose helium gas was passed through the titration system. It was also purchased from Proxair. All solutions were prepared in nanopure water. The indicator, murexide, was added in solid form and it was mixed with potassium nitrate for stabilisation as discussed in Chapter 2, Section 2.3.1. This indicator mixture was always used in each titration. Concentrated ammonia was used as buffer to make the pH 11.8. To a 50.0 mL of sample solution 5 mL of ammonia was added and concentration of ammonia in the final volume was 1.4M.

6.2.2 APPARATUS

A schematic diagram of the titration system is shown in Figure 6.1. The solution in the beaker was constantly stirred by a magnetic stirrer and the solution was pumped to the diode array spectrophotometer by a peristaltic pump operated with tygon pump tubing. The beaker containing silver solution was closed with a specially made teflon lid. Holes were made on it to provide circulation of solution and helium, and one hole held the micro burette containing titrant. There were two lines of teflon connecting tubing for the circulation of solution in and out of the spectrophotometer. Teflon tubing are permeable to air. Therefore, they were covered with tygon tubings. Helium gas was passed through the solution through a teflon tubing covered with tygon to offer an air free atmosphere. The details of the spectrometer and peristaltic pumps were already discussed

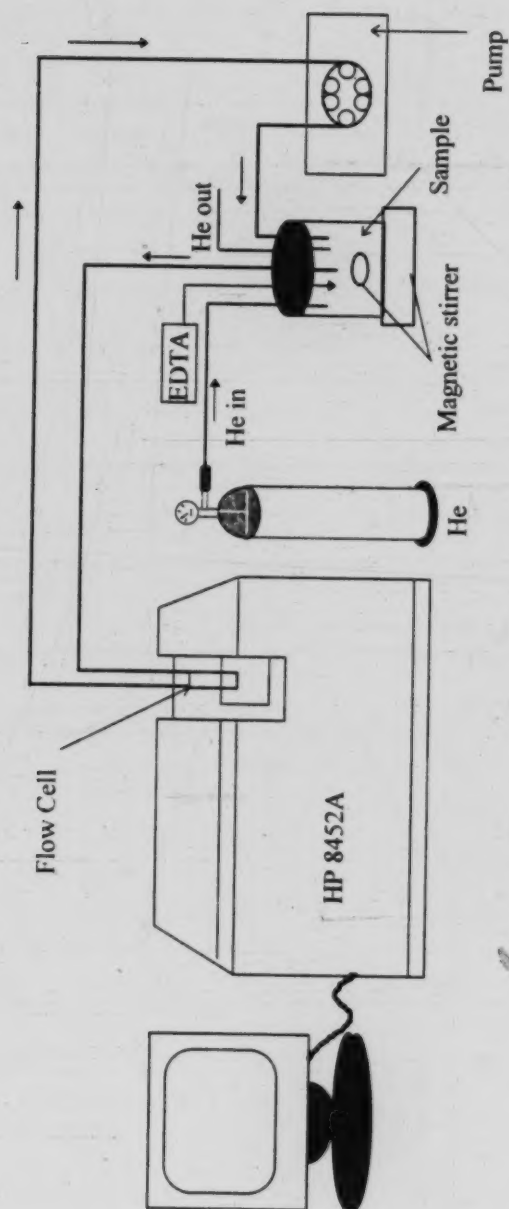


Figure 6.1 : A schematic representation of titration system.

in Chapter 2, Section 2.3.3. The resulting spectrum was displayed by HP 89532A MS-DOS UV-Visible General Scanning Software.

6.2.3 EXPERIMENTAL PROCEDURE

6.2.3.1 TITRATION OF SILVER POWDER WITH EDTA

To 25-30 mg of accurately weighed potassium tetracyanonickelate, was added 5 ml of concentrated ammonia (14.5M) and everything was dissolved in 45 ml of nano pure water. Helium gas was purged through the solution for 15 minutes. The spectrum of the solution was taken. The bottle containing silver powder was opened in a glove bag filled with nitrogen to prevent oxidation and about 18 mg of accurately weighed Ag(0) was transferred into a vial. Then silver powder was transferred into the solution and was purged with helium. About 8 mg of murexide was added and titrated with 0.01007M EDTA until no changes in absorbance was observed. The solution was continuously stirred using a magnetic stirrer. The empty vial was weighed and the difference in weight would be the weight of silver powder added. Another titration was carried out without bubbling helium through the solution to prove that purging helium through the solution effectively prevent air oxidation of silver powder.

6.2.3.2 TITRATION OF A SYNTHETIC MIXTURE OF SILVER(I) AND SILVER(0) WITH EDTA

To 60-70 mg of accurately weighed potassium tetracyanonickelate, added 5 mL of concentrated ammonia (14.5M), 1.300 mL of 0.1M silver nitrate using a micro pipette, 10.013 mL of 2.38×10^{-4} M Ag^+ from silver oxide solution prepared as discussed in Chapter 5, Section 5.3.1. The solution was delivered by a calibrated 10 mL pipette. Then 34.0 mL of nanopure water was added through a 50.0 mL graduate cylinder. Helium gas was purged for 15 minutes and added 15-20 mg of accurately weighed silver powder. Finally about 8 mg of murexide was added. EDTA was added from a 2.00 mL micro burette and taken the spectrum at 550 nm after each addition of EDTA. The solution was stirred continuously with a magnetic stirrer and at least one minute was allowed for complete mixing after each successive addition of EDTA and all titration were completed within thirty minutes to avoid decomposition of indicator. EDTA was added until no change in absorbance was observed.

6.3 RESULTS AND DISCUSSION

6.3.1 TITRATION OF SILVER POWDER

Examination of Figure 6.2 reveals that there was no free nickel titrated by EDTA, otherwise there would be a part in the graph where there was zero slope or only a small one during the initial addition of EDTA as eluded to earlier in Chapter 3, Section 3.4. The added EDTA complexed with nickel in nickel-murexide complex and nickel-ammine complexes. This step was accompanied by much larger change in absorbance due to the murexide liberated from nickel-murexide complex. After the end point there was no change in absorbance. The end point was determined by interpolation of two straight line portions and the point of intersection was chosen as end point as shown in Figure 6.2. The data for the titration is tabulated in Table B 6 in Appendix B. Silver was added in elemental form, hence the volume of EDTA used was for titrating nickel released in the presence of blank alone. But it was found that volume of EDTA used was more than that expected for a blank situation. The difference in volume of EDTA consumed corresponds to Ag(I) present in the solution. The only source of Ag(I) is silver powder. Silver powder was weighed in an air free atmosphere and the sample solution was purged with helium all the time. Therefore the chances of air oxidation was minimum in this case. Elemental silver that was added was in powdered form. There was a possibility of silver oxide

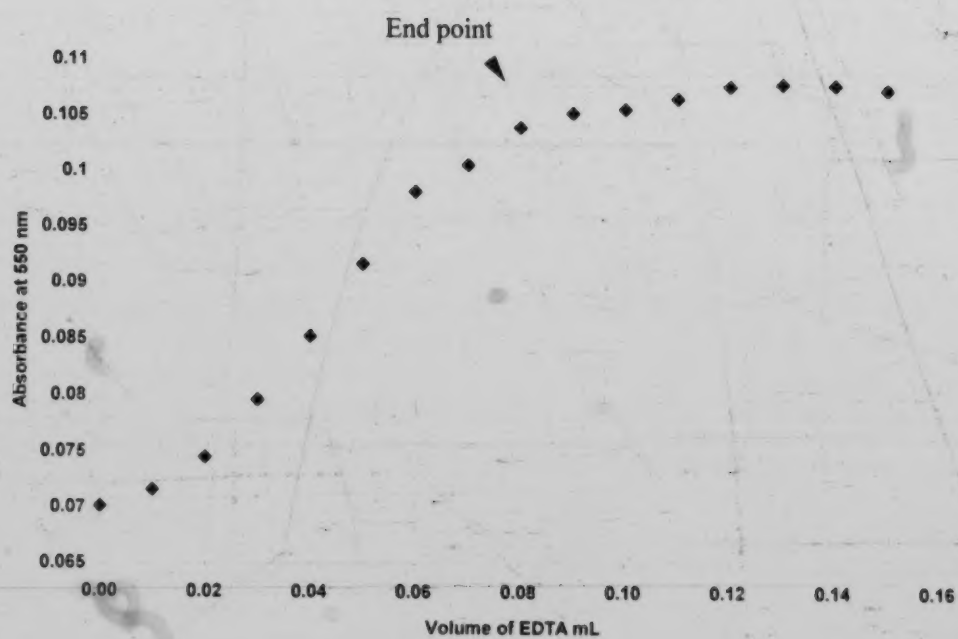


Figure 6.2: Titration of silver powder: The sample solution contains 62 mg of Ag(0),

~ 8 mg murexide and 3.6×10^{-3} M $K_2Ni(CN)_4$ in 1.4M ammonia as buffer.

Volume of 0.01007M EDTA used at the end point was 0.073 mL.

present in thin layer around each particle of Ag(0). Hence the source of Ag(I) may be this silver oxide layer. The experimental results are shown in Table 6.1. Potassium tetracyanonickelate and silver were added in solid form. Therefore their weight were different in each individual run. Figure 6.2 shows that there was no free nickel. Color of the solution before the addition of Ag(0) was purple due to the presence of murexide. Its color did not change to golden yellow after the addition of Ag(0) but it changed to a less purple color. These observations concludes that there was still free murexide present in the solution after the addition of silver powder. The blank correction $C_{\text{Ni, blank}}$ that is calculated theoretically in Chapter 3, Section 3.2 is reproduced as follows,

$$[\text{CN}^-]^5 = 4[\text{Ni}(\text{CN})_4^{2-}] \times 1.31 \times 10^{-31} \{1 + 2.87 \times 10^9 + 4.3 \times 10^{15} [\text{H}_2\text{In}^{3-}]\} \dots\dots\dots (6.1)$$

$$C_{\text{Ni, blank}} = \frac{[\text{CN}^-]}{4} \dots\dots\dots (6.2)$$

The concentration of free murexide was determined by the simultaneous analysis of wavelength at 500 and 550 nm as discussed in Chapter 3, Section 3.2, equations (3.7) and (3.8). Experimentally total concentration of nickel that was not bound to cyanide was determined by the following equation,

$$C_{\text{Ni}} = \frac{\text{Vol}_{\text{EDTA}} \times M_{\text{EDTA}}}{\text{Volume of sample solution}} \dots\dots\dots (6.3)$$

Therefore concentration of Ag(I), C_{Ag} , and % Ag(I) present in silver powder are determined by the following equations,

$$C_{Ni} = \frac{[Ag^+]}{2} + C_{Ni, blank} \dots\dots\dots(6.4)$$

$$\text{Percentage of Ag(I) present in silver powder} = \frac{\text{moles of Ag(I) found}}{\text{moles of Ag(0) added}} \times 100 \dots\dots\dots(6.5)$$

The difference between theoretical and experimental result corresponds to concentration of Ag(I) present in the solution. For example, taking the first set of data in Table 6.1,

$C_{Ni, blank}$ found theoretically is $9.35 \times 10^{-6}M$ and that found experimentally is

$1.47 \times 10^{-5}M$. Therefore concentration of Ag(I) present in the solution = $2(1.47 \times 10^{-5} -$

$9.35 \times 10^{-6})M$ which corresponds to 5.31×10^{-7} moles or 5.73×10^{-5} g of silver. Total

concentration of Ag(0) was 6.234×10^{-2} g. Therefore percentage of Ag(I) present

was 0.1%. It was found that the percentage of Ag(I) present was 0.1% regardless of weight

of silver powder taken. Ag(0) was purchased from Aldrich and the manufacturer claim a

purity of 99.9% which was consistent with the experimental result.

The same experiment was carried out without purging helium through the sample solution. The titration was not completed even after twice the amount of EDTA was used.

The dissolution of Ag (0) to Ag(I) was rather slow and titration was not completed even

after 30 minutes. The experiment should be completed within 30 minutes otherwise

indicator murexide dissociate in alkaline medium. Therefore, purging helium through the

solution was an effective way of preventing air oxidation of Ag(0).

Data No.	Abs at 500 nm before adding silver or EDTA	Abs at 550 nm before adding silver or EDTA	Concentration of free murexide (M)	Molarity of $K_2Ni(CN)_4$ (M)	Volume of EDTA used (mL) ± 0.001
1	0.098 ₄	0.083 ₅	8.88×10^{-6}	3.58×10^{-3}	0.073
2	0.057 ₉	0.046 ₅	4.91×10^{-6}	2.25×10^{-3}	0.047 ₆
3	0.067 ₀	0.061 ₄	6.61×10^{-6}	3.29×10^{-3}	0.055

Table 6.1 Results of titration of Ag(0) with EDTA in the absence of air: Concentration of free murexide was calculated using equations (3.7) and (3.8).

Data No.	Weight of silver added (g)	$C_{\text{Ni, blank}}$ theoretically $(M) \times 10^{-6}$	$C_{\text{Ni, blank}}$ experimentally $(M) \times 10^{-5}$	Concentration of silver(I) in the solution $(M) \times 10^{-5}$	No. of moles of silver(I) $\times 10^{-7}$	% of Ag(I)
1	0.06234	9.44	1.47 ± 0.04	1.05 ± 0.04	5.25	0.09
2	0.01808	7.72	0.941 ± 0.03	0.337 ± 0.03	1.68	0.1
3	0.03037	8.79	1.11 ± 0.03	0.462 ± 0.03	2.31	0.08

Table 6.2: Results of determination of percentage of Ag(I) present in Ag(0) powder: Theoretically

$C_{\text{Ni, blank}}$ was calculated using equation (6.1) and (6.2) and experimentally it was calculated using equation (6.3). The concentration of Ag(I) and % of Ag(I) were calculated using equations (6.4) and (6.5) respectively.

6.3.2 TITRATION OF SYNTHETIC MIXTURE OF Ag (0) AND Ag(I)

The titration curve for synthetic mixture of Ag(I) and Ag(0) with EDTA is shown in Figure 6.3. Examination of this figure indicates that during initial addition of EDTA free nickel was complexed first (region 'a'). Therefore during this part there was no appreciable change in absorbance was observed. Once all free nickel was used up, EDTA started to react with nickel in nickel-murexide complex and nickel-ammine complexes (region 'b'). This step was associated with a large change in absorbance. After all nickel was displaced there was no change in absorbance was observed (region 'c'). In this case Ag(I) concentration was in the range of $2.3 \times 10^{-3} \text{M}$ which was higher than that used for the experiments in Chapter 5. Hence in region 'c' less curvature was occurred. Silver powder was added in such a ratio that 50-65% of total silver exist as Ag(0). All titrations were carried out within 30 minutes. Figure 6.3 shows the shape of titration curve for the synthetic mixture of Ag(I) and Ag(0) with EDTA in the presence of NaCl. The data for these titrations are tabulated in Table B 7 and B 8 in the Appendix B. The results of titrations of synthetic mixtures of Ag(I) and Ag(0) with EDTA in the absence and in the presence of NaCl are shown in Table 6.3 and Table 6.4 respectively.

Potassium tetracyanonickelate and Ag(0) were added in solid form. Therefore their amount varies among each run. Total number of moles of Ag(I) added was calculated including Ag(I) from Ag(0) accounting 0.1% of Ag(0) exist as Ag(I). The concentration of silver was calculated experimentally using equations (6.3) and

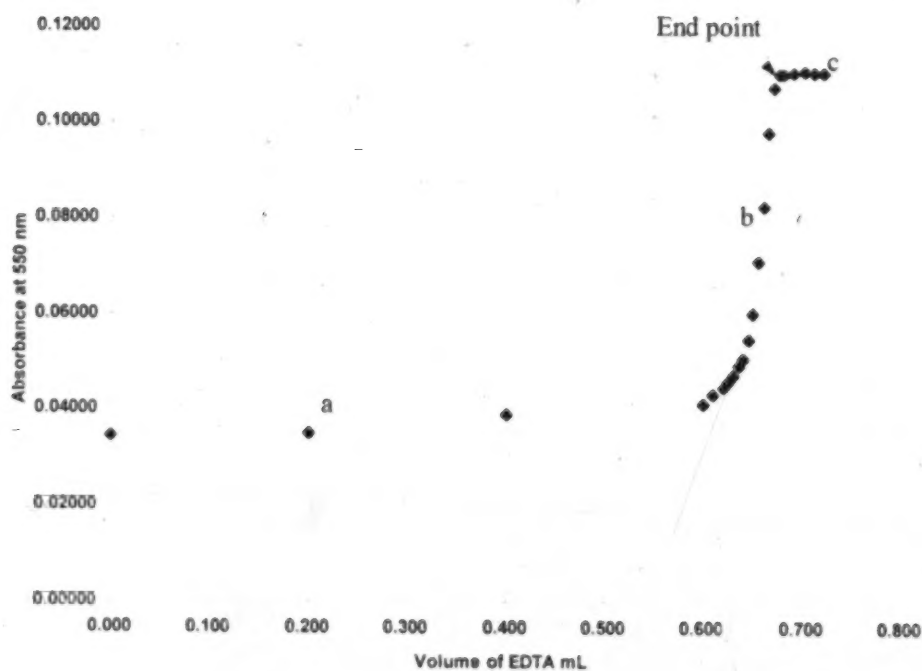


Figure 6.3: Titration of synthetic mixture of Ag(0) and Ag(I): The solution contains 1.3 mL of 0.1001M AgNO_3 , 10.012 mL of $2.377 \times 10^{-4}\text{M}$ Ag^+ from Ag_2O , 14.86 mg of Ag(0), $8.0 \times 10^{-4}\text{M}$ $\text{K}_2\text{Ni}(\text{CN})_4$ and about 10 mg of murexide in 1.4M ammonia as buffer. Volume of 0.1003M EDTA used at the end point was 0.667 mL.

(6.4). Comparison of total number of moles of Ag(I) added with the experimental result shows that they agree quite well.

The results in Table 6.5 shows the titration of the same species in the presence of 0.15M NaCl. We could see that comparison of total number of moles of Ag(I) added with the experimental result were in good agreement in the presence of halide ions too. These titrations proved that indirect titration of silver with EDTA can account all species of Ag(I). An added benefit of this procedure was there was no need to run a blank titration in order to account the blank. By knowing exact amount of solid tetracyanonickelate added a proper blank correction could be made with the aid of equations (5.8) and (5.9). This was already proved in the results tabulated in Table 5.1 and Table 5.2 in Chapter 5.

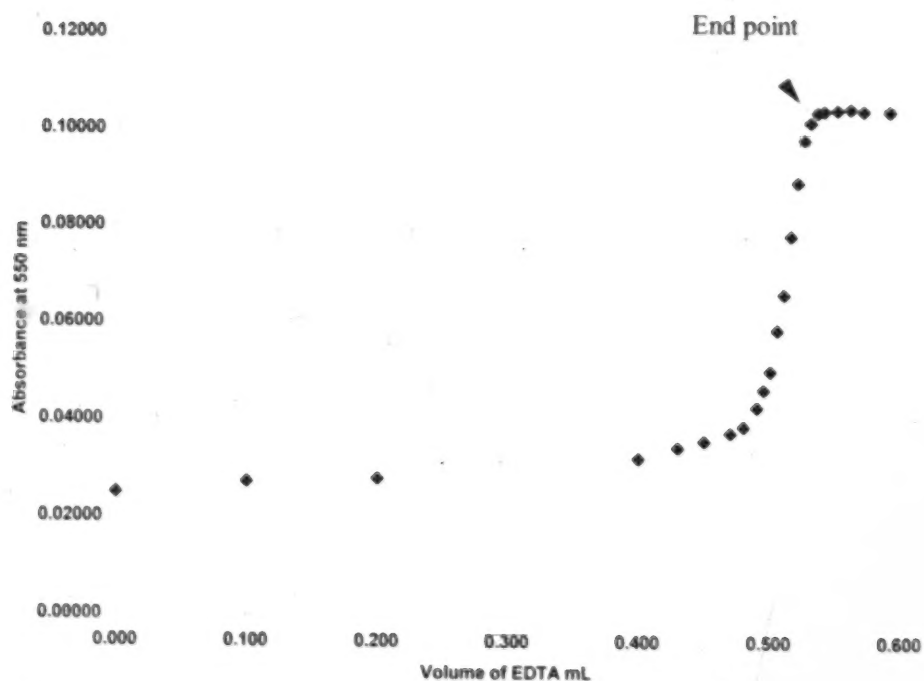


Figure 6.4: Titration of synthetic mixture of Ag(0) and Ag(I) in the presence 0.15M NaCl:

The solution contains 1.020 mL of 0.1001M AgNO₃, 10.012 mL of 2.377×10^{-4} M Ag⁺ from Ag₂O, 28.55 mg of Ag(0), 0.15M NaCl, 8.24×10^{-4} M K₂Ni(CN)₄ and about 10 mg of murexide in 1.4M ammonia as buffer. Volume of 0.1003M EDTA used at the end point was 0.526 mL.

Data No	Total number of moles of $K_2Ni(CN)_4 \times 10^{-4}$	Volume of 0.1001M silver nitrate (mL)	Volume of $2.377 \times 10^{-4}M Ag^+$ from Ag_2O (mL)	Weight of $Ag(0)$ at (g)
1	4.003	1.3	10.013	0.01486
2	3.380	1.34	10.013	0.02456
3	1.374	1.34	10.013	0.02419

Table 6.3: Data for the titration of synthetic mixture of $Ag(0)$ and $Ag(I)$ with EDTA. A 50.0 (± 0.6) mL of sample solution contains Ag^+ , $Ag(0)$, ~ 10 mg of murexide and the pH was adjusted to 11.8 by adding 5.0 (± 0.1) mL of concentrated ammonia (14.5M).

Data No	Volume of EDTA used at the end point (mL)	Blank correction (mL)	Total moles of Ag^+ added	Total moles of Ag^+ found
1	0.667	0.003	0.000133	0.000133
2	0.673	0.003	0.000137	0.000134
3	0.685	0.003	0.000137	0.000137

Table 6.4: Results of titration of synthetic mixture of $Ag(0)$ and $Ag(I)$ with 0.1003M

EDTA: The blank correction was calculated using equations (5.8) and (5.9) and total moles of Ag^+ calculated experimentally using equations (5.5) and (5.6).

Data No	Total number of moles of $\text{K}_2\text{Ni}(\text{CN})_4 \times 10^{-4}$	Volume of 0.1001M silver nitrate (mL)	Volume of $2.377 \times 10^{-4}\text{M}$ Ag^+ from Ag_2O (mL)	Weight of $\text{Ag}(0)$ added (g)
1	4.003	1.020	10.013	0.02855
2	3.380	1.310	10.013	0.02704
3	1.374	1.300	10.013	0.02769

Table 6.5: Data for the titration of synthetic mixture of $\text{Ag}(0)$ and $\text{Ag}(I)$ with EDTA in the presence of 0.15M NaCl. A 50.0 (± 0.6) mL of sample solution contains Ag^+ , $\text{Ag}(0)$, ~ 10 mg of murexide and the pH was adjusted to 11.8 by adding 5.0 (± 0.1) mL of concentrated ammonia (14.5M).

Data No	Volume of EDTA used at the end point (mL)	Blank correction (mL)	Total moles of Ag^+ added	Total moles of Ag^+ found
1	0.526	0.003	0.000105	0.000105
2	0.656	0.003	0.000134	0.000131
3	0.673	0.002	0.000136	0.000134

Table 6.6: Results of titration of synthetic mixture of $\text{Ag}(0)$ and $\text{Ag}(I)$ with 0.1003M EDTA in the presence of 0.15M NaCl: The blank correction was calculated using equations (5.8) and (5.9) and total moles of Ag^+ calculated experimentally using equations (5.5) and (5.6).

Silver coated nylon fabrics are widely used to treat and manage post operative debridement of wounds. The release of silver from the coatings may be in various forms of silver. In the proposed method concentration of Ag(I) was determined quantitatively in the presence of Ag(0) . The procedure is simple, fast and reproducible.

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APPENDICES

This section contains :

Appendix A : Figures for finding molar absorptivities

Appendix B : Data tables for the figures in the thesis and for Appendix A

APPENDIX A

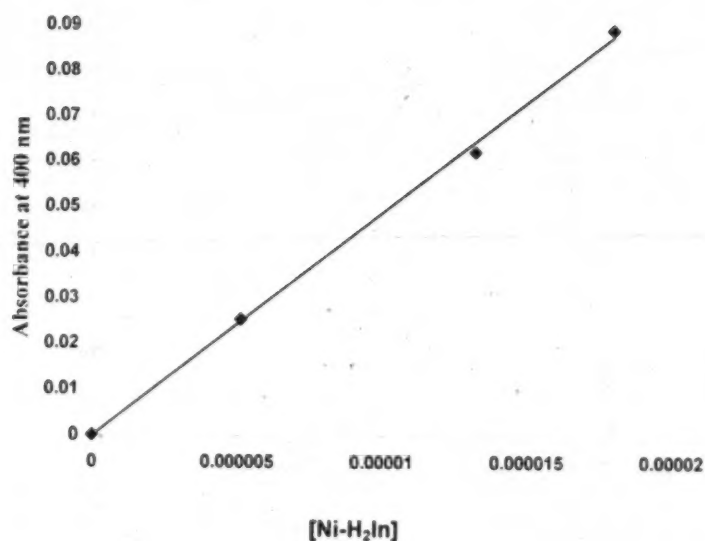


Figure A 1 : Determination of molar absorptivity of nickel-murexide complex at 400 nm by plotting absorbance vs concentration of nickel - murexide; The sample solution contains nickel- murexide complex and 1.4M ammonia was used to adjust the pH to 11.8. Molar absorptivity (4900) was determined from the slope.

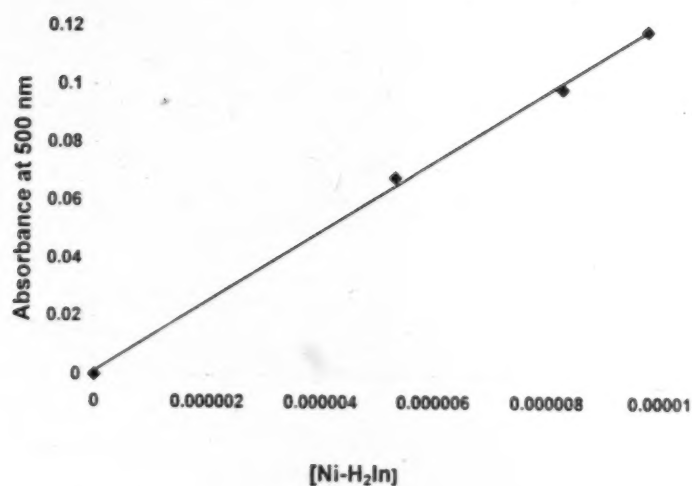


Figure A 2 : Determination of molar absorptivity of nickel-murexide complex at 500 nm by plotting absorbance vs concentration of nickel-murexide complex ; The sample solution contains nickel- murexide complex and 1.4M ammonia was used to adjust the pH to 11.8. Molar absorptivity (12000) was determined from the slope.

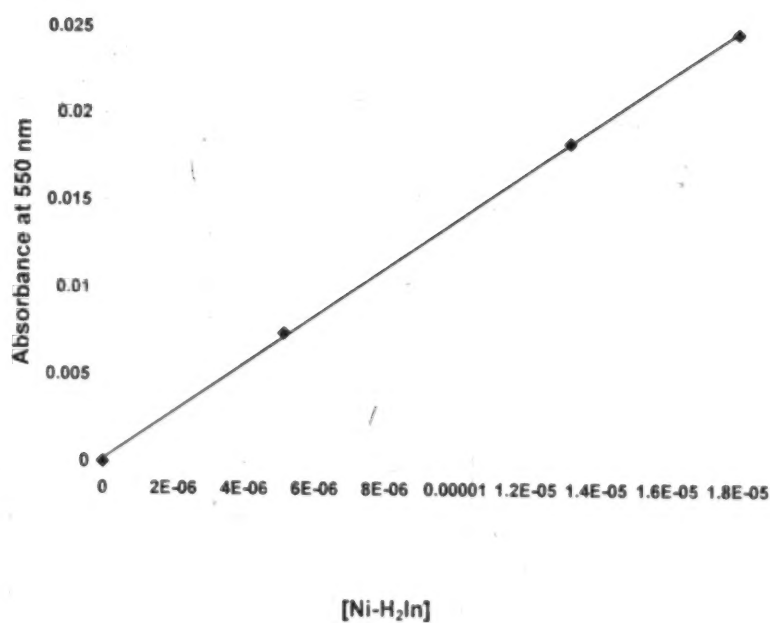


Figure A 3 : Determination of molar absorptivity of nickel-murexide complex at 550 nm by plotting absorbance vs concentration of nickel murexide complex. The sample solution contains nickel- murexide complex and 1.4M ammonia was used to adjust the pH to 11.8. Molar absorptivity (1400) was determined from the slope.

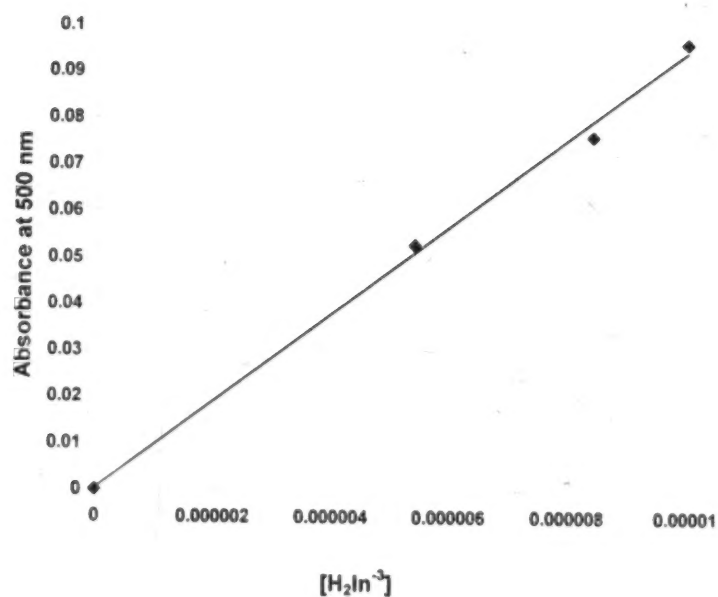


Figure A 4 : Determination of molar absorptivity of murexide at 500 nm by plotting absorbance vs concentration of murexide; The sample solution contains murexide and 1.4M ammonia was used to adjust the pH to 11.8. Molar absorptivity (9400) was determined from the slope.

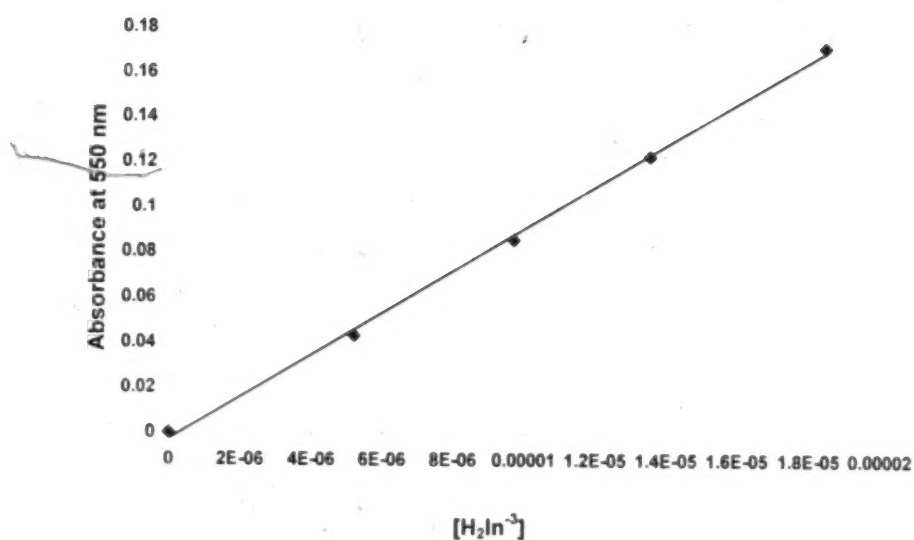


Figure A 5 : Determination of molar absorptivity of murexide at 550 nm by plotting absorbance vs concentration of murexide; The sample solution contains murexide and 1.4M ammonia was used to adjust the pH to 11.8. Molar absorptivity (9300) was determined from the slope.

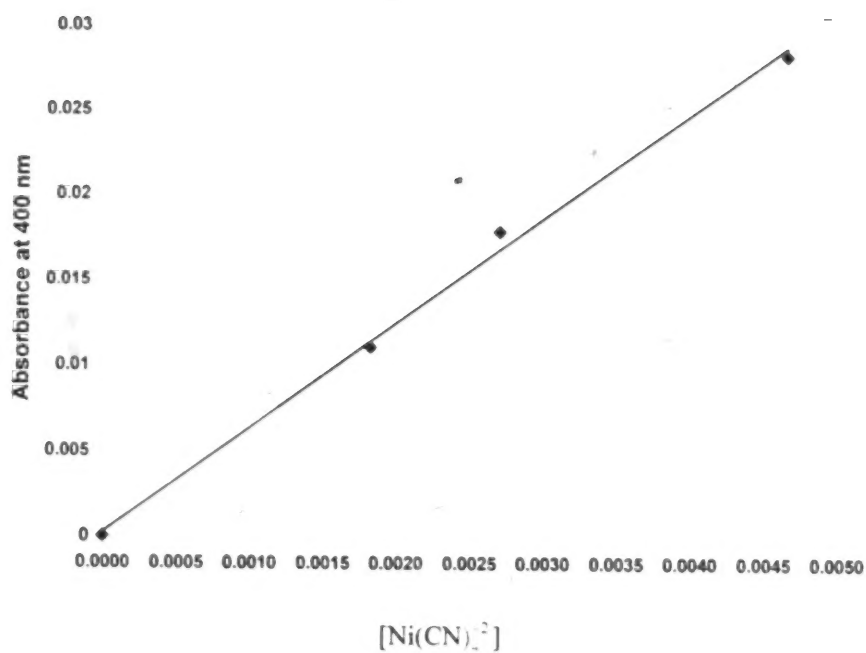


Figure A 6 : Determination of molar absorptivity of potassium tetracyanonickelate at 400 nm by plotting absorbance vs concentration of potassium tetracyanonickelate; The sample solution contains murexide and 1.4M ammonia was used to adjust the pH to 11.8. Molar absorptivity (6.0) was determined from the slope.

APPENDIX B

Table B 1 : Stability of murexide with time : Data for Figure 2.6

Time (minutes)	Absorbance at 550 nm
0.00	0.067 ₄
1.50	0.067 ₅
3.15	0.067 ₄
4.37	0.066 ₉
6.23	0.066 ₉
7.46	0.066 ₆
10.00	0.066 ₃
12.51	0.066 ₂
14.42	0.066 ₁
16.53	0.065 ₇
19.29	0.065 ₂
22.13	0.064 ₂
24.53	0.062 ₇
28.45	0.062 ₂
30.30	0.062 ₁
33.43	0.058 ₉
35.43	0.058 ₈
38.23	0.056 ₄
45.00	0.054 ₃

Table B 2 : Blank titration: Data for figure 3.1

Volume of EDTA (mL)	Absorbance at 550 nm
0.000	0.041 ₆
0.013	0.042 ₂
0.022	0.043 ₁
0.033	0.046 ₁
0.039	0.048 ₀
0.047	0.050 ₀
0.057	0.052 ₃
0.068	0.054 ₁
0.078	0.055 ₃
0.093	0.057 ₀
0.105	0.057 ₄
0.117	0.057 ₅
0.126	0.057 ₅
0.134	0.057 ₈
0.200	0.057 ₈
0.300	0.057 ₈

Table B 3 : Spectrophotometric titration of silver nitrate with EDTA : Data for Figure 5.2

Volume of EDTA (mL)	Absorbance at 550 nm
0.000	0.012 ₃
0.100	0.013 ₆
0.200	0.017 ₁
0.242	0.020 ₉
0.280	0.031
0.300	0.039 ₇
0.306	0.042 ₇
0.310	0.044 ₇
0.315	0.049 ₂
0.320	0.050 ₈
0.324	0.053 ₈
0.330	0.056 ₇
0.336	0.060 ₁
0.340	0.062 ₂
0.344	0.063 ₇
0.348	0.065 ₇
0.350	0.065 ₉
0.356	0.068 ₉
0.362	0.071 ₄
0.368	0.074 ₂
0.374	0.076 ₁
0.378	0.076 ₆
0.384	0.077 ₈
0.388	0.077 ₉
0.394	0.078 ₆
0.400	0.079 ₀
0.420	0.079 ₃
0.460	0.079 ₇
0.480	0.079 ₃

Table B 4: Spectrophotometric titration of silver nitrate with EDTA in the presence of
0.15M NaCl: Data for Figure 5.3

Volume of EDTA (mL)	Absorbance at 550 nm
0.000	0.014 ₉
0.100	0.016 ₁
0.200	0.01 ₈
0.220	0.018 ₈
0.240	0.020 ₃
0.260	0.022 ₂
0.280	0.025 ₁
0.290	0.028 ₀
0.300	0.031 ₆
0.310	0.034 ₅
0.320	0.039 ₃
0.330	0.043 ₈
0.340	0.049 ₀
0.350	0.054 ₃
0.360	0.057 ₀
0.365	0.058 ₉
0.370	0.061 ₈
0.375	0.062 ₄
0.380	0.063 ₈
0.390	0.064 ₈
0.400	0.066 ₁
0.410	0.066 ₂
0.420	0.066 ₂
0.430	0.066 ₁

Table B 5 : Spectrophotometric titration of silver oxide with EDTA : Data for Figure 5.4

Volume of EDTA (mL)	Absorbance at 550 nm
0.00	0.012 ₀
0.10	0.011 ₄
0.20	0.012 ₄
0.30	0.014 ₇
0.40	0.018 ₇
0.45	0.022 ₇
0.50	0.030 ₃
0.52	0.035 ₃
0.53	0.038 ₀
0.55	0.044 ₂
0.56	0.048 ₁
0.57	0.052 ₄
0.58	0.056 ₂
0.59	0.060 ₄
0.6	0.064 ₁
0.61	0.067 ₆
0.62	0.070 ₃
0.63	0.073 ₁
0.64	0.075 ₁
0.65	0.077 ₁
0.66	0.078 ₁
0.67	0.078 ₇
0.68	0.079 ₃
0.69	0.079 ₃
0.7	0.079 ₂
0.72	0.079 ₃

Table B 6 : Spectrophotometric titration of silver powder with EDTA : Data for

Figure 6.2

Volume of EDTA (mL)	Absorbance at 550 nm
0.00	0.042 ₀
0.01	0.043 ₁
0.02	0.050 ₀
0.03	0.056 ₂
0.04	0.060 ₅
0.05	0.062 ₉
0.06	0.064 ₄
0.07	0.065 ₃
0.08	0.065 ₆
0.09	0.065 ₈
0.10	0.065 ₇

Table B 7 : Spectrophotometric titration of synthetic mixture of Ag(0) and Ag(I) with

EDTA : Data for Figure 6.3

Volume of EDTA (mL)	Absorbance at 550 nm
0.000	0.034 ₃
0.200	0.035
0.400	0.039
0.600	0.041 ₃
0.610	0.043 ₃
0.620	0.044 ₆
0.625	0.045 ₉
0.630	0.047 ₄
0.635	0.049 ₄
0.640	0.050 ₇
0.645	0.054 ₈
0.650	0.060 ₁
0.655	0.070 ₉
0.660	0.082 ₆
0.665	0.097 ₉
0.670	0.107 ₄
0.675	0.110 ₂
0.680	0.110 ₂
0.690	0.110 ₅
0.700	0.110 ₇
0.710	0.110 ₇
0.720	0.110 ₆

Table B 8 : Spectrophotometric titration of synthetic mixture of Ag(0) and Ag(I) with EDTA in the presence of 0.15M NaCl : Data for Figure 6.4

Volume of EDTA (mL)	Absorbance at 550 nm
0.000	0.025 ₀
0.100	0.027 ₃
0.200	0.028 ₀
0.400	0.032 ₂
0.430	0.034 ₄
0.450	0.035 ₉
0.470	0.037 ₅
0.480	0.038 ₉
0.490	0.042 ₈
0.495	0.046 ₅
0.500	0.050 ₃
0.505	0.058 ₇
0.510	0.066 ₁
0.515	0.078 ₂
0.520	0.089 ₃
0.525	0.098 ₂
0.530	0.101 ₈
0.535	0.103 ₈
0.540	0.104 ₂
0.550	0.104 ₄
0.560	0.104 ₇
0.570	0.104 ₂
0.590	0.104 ₁

Table B 9: Molar absorptivity coefficient of Ni-murexide complex at 400 nm: Data for

Figure A1

Concentration (M)	Absorbance at 400 nm
5.13×10^{-6}	0.025 ₃
1.32×10^{-5}	0.062 ₁
1.80×10^{-6}	0.089 ₀

Table B10: Molar absorptivity coefficient of Ni-murexide complex at 500 nm: Data for

Figure A2

Concentration (M)	Absorbance at 500 nm
5.30×10^{-6}	0.068 ₀
8.25×10^{-5}	0.098 ₆
9.74×10^{-6}	0.118 ₈

Table B11: Molar absorptivity coefficient of Ni-murexide complex at 550 nm: Data for

Figure A3

Concentration (M)	Absorbance at 550 nm
5.13×10^{-6}	0.007 ₄
1.32×10^{-5}	0.018 ₃
1.80×10^{-6}	0.024 ₇

Table B12 : Molar absorptivity coefficient of murexide at 500 nm: Data for Figure A 4

Concentration (M)	Absorbance at 500 nm
5.40×10^{-6}	0.052 ₇
8.40×10^{-6}	0.076 ₁
9.98×10^{-6}	0.096 ₃

Table B13 : Molar absorptivity coefficient of murexide at 550 nm: Data for Figure A 5

Concentration (M)	Absorbance at 550 nm
5.40×10^{-6}	0.043 ₀
8.40×10^{-6}	0.122 ₇
9.98×10^{-6}	0.171 ₄

Table B14 : Molar absorptivity coefficient of $K_2Ni(CN)_4$ at 400 nm: Data for Figure A 6

Concentration (M)	Absorbance at 400 nm
5.40×10^{-6}	0.011 ₀
8.40×10^{-6}	0.017 ₈
9.98×10^{-6}	0.028 ₂